1966

The Effect of a Second Order Chemical Reaction on the Absorption of Methyl Mercaptan in a Laminar Liquid Jet.

Joseph Earl Landry
Louisiana State University and Agricultural & Mechanical College

THE EFFECT OF A SECOND ORDER CHEMICAL REACTION ON THE ABSORPTION OF METHYL MERCAPTAN IN A LAMINAR LIQUID JET

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirement for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Joseph Earl Landry
B.S., University of Southwestern Louisiana, 1958
M.S., Louisiana State University, 1963
August, 1966

ACKNOWLEDGEMENTS

The author expresses his sincerest thanks and appreciation to Professor Jesse Coates, for his direction, assistance, and understanding. The advice of the other members of the Faculty in Chemical Engineering is also gratefully acknowledged. The assistance of the National Council for Stream Improvement (of the Pulp, Paper, and Paperboard Industries), particularly the kind understanding of Mr. Herbert Berger, is recognized and appreciated. Deserving particular mention are, Mr. John Miller, for his assistance in evaluation of the equipment, Mr. L. M. Carpenter for his assistance in fabricating the experimental equipment, the staff of the University's Computer Research Center for their assistance in processing the mathematical computations, and Mrs. Lee M. Potzner and Mr. Norman D. Hyett for their assistance in the preparation of the manuscript.

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ABSTRACT

Present knowledge in the field of gas absorption with simultaneous chemical reaction has not been advanced to the point where commercial absorbers can be designed routinely. Pilot scale studies can not be scaled up using the conventional concepts of physical gas absorption, unless the process is gas phase limiting throughout the packed absorber. A review of the literature indicates the need for additional experimental data in the absorption of methyl mercaptan in aqueous sodium hydroxide solutions. These data are needed for air pollution control in the paper industry. Further, there is need for testing the mathematical solutions published for the penetration theory with chemical reaction and extension of these concepts for the design and scale-up of equipment.

The laminar liquid jet was chosen to obtain the basic absorption data on the methyl mercaptan-sodium hydroxide system, because its unique fluid dynamic and operating characteristics allow the use of the penetration theory for the description of the process. Further, the absorption data measured with the laminar jet can be analyzed to determine reaction rates for a postulated reaction mechanism.

The liquid jet formed by the diaphragm orifice is cylindrical and the boundary-layer effects caused by the orifice walls are minimal. Beyond the section of boundary layer retardation the jet

diameter can be predicted by the equations of motion for a frictionless jet.

The diffusion coefficients of carbon dioxide, sulfur dioxide, and methyl mercaptan in water at 25°C were measured. The gas absorption rates in the liquid jet follow the penetration theory results over the studied contact time range of 2.5 to 30 milliseconds. The measured values of the diffusion coefficients were comparable with reported results.

The absorption of methyl mercaptan in aqueous solutions of sodium hydroxide, as measured in the laminar liquid jet apparatus, were correlated by the penetration theory solutions for an infinitely fast irreversible reaction. The diffusion of the hydroxyl ion determines the effect on the mass transfer rate, which would differ significantly if the sodium hydroxide diffused as a molecular specie with its salt diffusivity.

The reaction of the dissolved methyl mercaptan with the hydroxyl ions is a very fast second order irreversible reaction with a forward rate constant in the order of 10^5 liters/gram-moles-second. The kinetics of this equation was inferred by extension of the penetration theory solutions in the parametric range studied.

The absorption of dilute gas solutions of methyl mercaptan in aqueous sodium hydroxide contacted in a packed absorber was predicted by a method of calculation based on the penetration theory. Knowing the reaction kinetics and the physical absorption constants the height of chemical absorbers can be calculated.

Dedicated to

my teachers,

my parents,

and my wife.

CHAPTER I

INTRODUCTION

Gas absorption is defined as an operation in which a gas is contacted with a liquid for purposes of dissolving one or more components of the gas and to provide a solution of these in the liquid. The transfer of the gaseous solute is a diffusional process. The molecules of the gas being absorbed have to pass by diffusion through the gas phase, cross the interface between gas and liquid, and then pass into the liquid phase. The molecules can move either by molecular diffusion, which is a slow process, or by eddy diffusion, a much faster process in which appreciable amounts of the liquid or gas move as in mixing. In order to increase the preferential solubility of the gas in the liquid, a compound is often added to the solvent which will react or otherwise form strong chemical bonds with the solute. The process is called chemical absorption or absorption accompanied with a chemical reaction.

The unit operation of chemical absorption is commercially important. Practical problems include the recovery of valuable or nuisance gases by continuous contact with a chemically active solvent. The selection of a solvent is based on economics. Solvent regenerability, costs of the solvent, quantity of solute used, and utilization of the spent solvent as a common process stream are factors to be considered.

Absorption systems with chemically reactive solvents are very important in the field of air pollution control and the chemical process industries. Typical problems of commercial importance are listed in Table 1. Note that most of the gaseous solutes listed in the table are also classed as air pollutants.

The need for controlling gaseous emissions to the environment is well documented and is becoming a national problem. Recent reports, such as the one by the President's Science Advisory Committee,[1] list the compounds which are of concern. Among gases which deterioate materials and degrade the environment are sulfur dioxide and hydrogen sulfide. Sulfur dioxide, accelerates the weathering of buildings and monuments. Urban concentration levels are high enough to endanger health. Hydrogen sulfide darkens paints containing lead and mercury, and also produce an unaesthetic air environment. Odors from organic sulfides and mercaptans also are nuisance.

The climatic effect of pollution is of some concern. Carbon dioxide is being added to the earth's atmosphere by the combustion of fossil fuel at the rate of 6 billion tons a year.[2] The report's projection for the year 2000 is a 25% increase in CO_2 over the present concentration level. It is claimed that this will modify the heat balance of the earth to such an extent that climatic changes will be chaotic and uncontrollable.

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[1] President's Science Advisory Committee, Restoring the Quality of Our Environment, Report of the Environmental Pollution Panel, November 1965.

[2] Ibid., p. 9.

TABLE I

ABSORPTION SYSTEMS WITH CHEMICAL REACTION[3]

Solute Gas	Reagent
CO_2	Carbonates
CO_2	Hydroxides
CO_2	Ethanolamines
CO	Cuprous amine complexes
CO	Cuprous ammonium chloride
SO_2	$Ca(OH)_2$
SO_2	Ozone - H_2O
SO_2	$HCrO_4$
SO_2	KOH
Cl_2	H_2O
Cl_2	$FeCl_2$
H_2S	Ethanol amines
H_2S	Hydroxides
H_2S	$Fe(OH)_3$
SO_3	H_2SO_4
C_2H_4	KOH
C_2H_4	Trialkyl phosphates
NO	$FeSO_4$
NO	$Ca(OH)_2$
NO	H_2SO_4
NO_2	H_2O

[3]A. J. Teller, "Absorption with Chemical Reaction," Chemical Engineering, July 11, 1961, p. 111.

The highest priority will be given to the investigation of effects and control measures pertaining to the following compounds:[4] sulfur dioxide, carbon monoxide, oxides of nitrogen, carcinogens, peracyl nitrates, gasoline additives including lead and asbestos particles. Compounds with high priority are: benzene and homologues, alkyl nitrates, alkyl nitrites, aldehydes, ethylene, pesticides, auto exhaust, amines, mercaptans, hydrogen sulfide, and beryllium particles.

While this all-encompassing report covers some distant goals, it points out the areas which will concern chemical engineers for the years ahead. It is a chemical engineering problem which is national in scope.

1. The Problem

The pulp and paper industry produces three important pollutants previously mentioned; sulfur dioxide, hydrogen sulfide, and methyl mercaptan. The compounds are by-products of combustion, hydrolysis, and delignification of wood with sodium hydroxide - sodium sulfide solutions. The removal of methyl mercaptan from process emissions will reduce the air pollution problems of the industry.

The subject of this study, sponsored by the National Council for Stream Improvement (of the Pulp, Paper, and Paperboard Industry) is the effect of chemical reaction on the absorption of methyl mercaptan in aqueous sodium hydroxide solutions. The scope of the study included the determination of the reaction mechanism, the rate of reaction, and the mass transfer variables. These variables were

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[4]Report of the Environmental Pollution Panel, op. cit., p. 66.

projected to pilot scale absorption systems as a demonstration of the design technique required for commercial application.

2. Technical Approach

The previous paragraphs cite the need for more efficient absorbers and makes it imperative to study the absorption processes from a fundamental point of view. The technology of chemical engineering is at a point where the design of absorbers for physical absorption is a nearly routine matter, when certain physical constants have been determined. Absorption with chemical reaction is much more complex and the design of absorbers not routine. Absorbers can be designed which will "work", but their performance cannot always be predicted. Goals of engineering studies should be the design of large scale equipment based on fundamental principles. This can be accomplished by the measurement of important physical variables and the development of a mathematical model (sets of predictive mathematical relationships) which can be used to describe the operation of the system.

The most widely used model for the interpretation of absorber performance is the Whitman[5] two film theory.[6] This model relies on the following series of assumptions:

1. Steady state conditions exist in both phases.
2. Rate of transfer is proportional to the concentration gradient.

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[5] W. G. Whitman, "The Two Film Theory of Gas Absorption," Chemical and Metallurgical Engineering, XXXIX, July 23, 1923, p. 146.

[6] This was later used to develop calculation techniques involving heights and number of mass transfer units.

3. Equilibrium exists between the liquid and vapor at the interface with no interfacial resistance to flow.

4. Hold up at the interface is negligible.

These assumptions led to the now familiar equations:

$$N_A = K_G a \ (p_G - p^*) \qquad (1\text{-}1a)$$

$$= K_L a \ (c^* - c_L) \qquad (1\text{-}1b)$$

$$= k_G a \ (p_G - p_i) \qquad (1\text{-}1c)$$

$$= k_L^o a \ (c_i - c_L) \qquad (1\text{-}1d)$$

These equations show an additivity of resistance similar to that used in heat and electrical conduction developments. The individual resistances are effectively combined into a single coefficient.

As a result of a search for a more realistic model of individual resistances, Higbie[7] developed the penetration theory. It removes the limitations (1) and (4) which are listed above, since it considers gas absorption into a quiescent liquid pool as an unsteady state mechanism. It has been found applicable to wetted-wall and packed columns, and was used recently to improve correlation the distillation

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[7] R. Higbie, "The Rate of Absorption of a Pure Gas into a Still Liquid during Short Periods of Exposure," A.I.Ch.E. Journal, XXXI (1935), p. 365.

tower tray efficiencies.[8] The difference in the theories concerns the dependence of the absorption coefficient on the diffusivity. The film theory indicates that;

$$k_L^o \alpha D_L \tag{1-2}$$

and the penetration theory's equivalent coefficient is;

$$k_L^o = 2\sqrt{\frac{D_L}{\pi t'}} \tag{1-3}$$

where t' is the time of contact. In a study by Sherwood and Hollaway,[9] the actual behavior in a packed tower was shown to be:

$$k_L \alpha \sqrt{D_L} \tag{1-4}$$

and not to the first power of the diffusion coefficient as the two film theory predicts.

If normal physical absorption were the only mechanism encountered the methods would be adequate using either the two film theory or the penetration theory. But in chemical absorption, the overall mass transfer coefficient varies widely because it is dependent on the

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[8] G. A. Hughmark, "Point Efficiencies for Tray Distillations," Chemical Engineering Progress, LXI, July 1965, p. 97.

[9] T. K. Sherwood and F. A. L. Hollaway, "Performance of Packed Towers - Liquid Film Data for Several Packings," Transactions of the American Institute of Chemical Engineers, XXXVI (1940), p. 39.

liquid phase reactant concentration; unless the major resistance to mass transfer is in the gas phase. The liquid phase resistance is a function of the reaction kinetics, which in turn may be limited by the rate of reaction or by the diffusion of the liquid phase reactant.[10] For systems in which the chemical reaction proceeds at a rate of the same magnitude as the mass transfer rate, the penetration theory is the best model. For very rapid irreversible reactions, the problem becomes a mass transfer problem where the transfer of liquid phase reactant must also be considered.

The problem of predicting the effect of simultaneous liquid-phase chemical reaction was approached early. Hatta[11] formulated a useful theory for describing absorption with very fast chemical reaction. This is a limiting case and not as general as the penetration theory approach.[12] Sherwood and Pigford[13] have reviewed the application of the two theories.

One of the drawbacks to the use of the penetration theory with chemical reaction is the complexity of the mathematical solutions.

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[10] J. H. Perry, Chemical Engineers' Handbook, (4th Edition; New York: McGraw-Hill, Inc., 1963), 14-19.

[11] S. Hatta, Technical Reports; Tohoku Imperial University, X (1932), p. 119, from Sherwood and Pigford (1952).

[12] P. L. T. Brian, J. F. Hurley, and E. H. Hasseltine, "Penetration Theory for Gas Absorption Accompanied by a Second Order Chemical Reaction," A.I.Ch.E. Journal, VII (1961), p. 227.

[13] T. K. Sherwood and R. L. Pigford, Absorption and Extraction, (2nd Edition; New York: McGraw-Hill, Inc., 1952), pp. 317-339).

Analytical solutions exist for two limiting cases, 1) pseudo first order reaction and, 2) second order, infinitely fast, irreversible reactions. For reaction rates other than those which are infinitely fast, the problem requires numerical solutions which are feasible only on high speed electronic computers with a relatively large memory. Within the last decade, the advent and general use of such machines has produced some general solutions. These are published for a wide range of parameters but are somewhat limited because of the small number of solutions given. Empirical correlations for these solutions have been developed. These solutions have been confirmed in a few cases. Vivian and King[13] cites the need for additional confirmation of theory by means of experimental research.

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[13] J. E. Vivian and C. J. King, Absorption and Distillation, Ch. 9 Vol. I, of Modern Chemical Engineering, ed. A. Acrivos (New York: Reinhold, Inc., 1960).

CHAPTER II

REVIEW OF RELATED RESEARCH

Although extensive work has been reported on absorption with chemical reaction in packed towers, only the area concerning models of known fluid dynamics will be considered as related research. A summary of published theoretical results on large scale chemical absorption will be given. The divisions of the related research area are patterned after Vivian and King[1] who have prepared the most recent compendium on gas absorption and distillation.

Vivian and King summarize the status of absorption theories and cites the following: 1) controlled absorption studies with chemical reaction are of value in providing basic mechanism information in chemical kinetics, 2) there is a need for testing the mathematical solutions given for the penetration theory approach, and 3) there is a need for extension of theory to large scale equipment. The following sections summarize the literature which is pertinent to this investigation.

1. Theoretical Studies

The text by Sherwood and Pigford[2] contains, in Chapter 9, the most

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[1] J. E. Vivian and C. J. King, Absorption and Distillation, Ch. 9, Vol. 1, of Modern Chemical Engineering, ed. A. Acrivos (New York: Reinhold, Inc., 1960).

[2] T. K. Sherwood and R. L. Pigford, Absorption and Extraction, (2nd Edition; New York: McGraw-Hill, Inc., 1952), pp. 317-339.

extensive summary of absorption accompanied by chemical reaction. The theoretical analysis has been expanded in recent years since the publication of the text, but it serves as a basis for understanding the steady state and unsteady state diffusion with chemical reaction. Application of the theory to large scale equipment could be updated, since some numerical solutions have been published in the last three years.

A more modern book by Bird, Stewart, and Lightfoot[3] include the basic concepts and the analytical solutions for two limiting cases of chemical absorption; pseudo first order and second order infinitely fast. The presentation of the mathematical derivation is lucid but the breadth of treatment of the subject was necessarily limited.

Levenspiel's[4] text on reaction engineering covers gas absorption with chemical reaction. The author uses a sample calculation of a packed tower to show the usefulness of the Hatta film theory, which he claims is accurate enough for packed tower design.

Many excellent papers have been published on the general theory of chemical absorption. The treatment by Danckwerts[5] adequately covers the subject while expanding on the use of the surface renewal theory. Danckwerts cited the need for improvement of the solutions since they had been good only for approximation and rough estimates.

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[3] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena (New York: John Wiley and Sons, Inc., 1960).

[4] O. A. Levenspiel, Chemical Reaction Engineering, (New York: John Wiley and Sons, Inc., 1962), p. 532.

[5] P. V. Danckwerts, "Gas Absorption Accompanied by Chemical Reaction," A.I.Ch.E. Journal, I (1955), p. 456.

Conventional absorption treatments fail because only two parameters, k_L and area are considered. Additional data on mechanism and physiochemical data should be coupled with mass transfer work. Danckwerts recommends that agitated liquid absorption work should be accompanied with measurement of transient absorption in the same liquids to remove many of the uncertainties present in the literature.

Toor and Chiang[6] discuss the similarity between the solutions of the film theory and penetration theory despite the very different pictures of the diffusion process given by the two models. For very fast reactions the writers propose the use of an effective diffusivity which represents the effect of reaction on absorption. The effective diffusivity is dependent on the liquid reactant concentration and offers no apparent usefulness over the solutions discussed below.

Huang and Kuo[7] have presented a general absorber model for first order irreversible chemical reaction. The authors used dimensionless groups to incorporate the film, penetration, and surface renewal theory in an absorber model. The technique should prove very useful in extension to large scale equipment when the reaction is first order, or pseudo first order. The authors state that with accurate values of physical absorption coefficients the effect of reaction on mass transfer rate can accurately be predicted.

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[6] H. L. Toor and S. H. Chiang, "Diffusion-Controlled Reactions," A.I.Ch.E. Journal, V (1959), p. 339.

[7] C. Huang and C. Kuo, "General Mathematical Model for Mass Transfer Accompanied by Chemical Reaction," A.I.Ch.E. Journal, IX (1963), p. 161.

Considering the existence of two analytical solutions for limiting cases, there is much need for some generalized solutions describing moderate rate, second order reactions. The development of numerical solutions for second order non-linear partial differential equations became feasible with the development of high speed digital computers with large memory cores. Brian, Hurley, and Hasseltine[8] have published a solution to the penetration theory for a second order irreversible reaction. The solution of the equations, which will be described in Chapter IV, are presented in the form of generalized curves. The usefulness of the numerical solutions to the penetration theory was extended when Brian[9] published the results for a general order kinetic reaction. The use of a dimensionless parameter, M, which is the function of the reaction rate constant and the contact time, renders the solution insensitive to the order of the reaction. Therefore, the generalized plots are versatile for any order. Four plots are presented which cover three initial liquid phase reactant concentrations, with each plot covering several orders of reaction. The practical or useful result of all these solutions is a correlative equation which can be used to interpolate or to predict the numerical solutions with very good accuracy.

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[8] P. L. T. Brian, J. F. Hurley, and E. H. Hasseltine, "Penetration Theory for Gas Absorption Accompanied by a Second Order Chemical Reaction," A.I.Ch.E. Journal, VII (1961), p. 227.

[9] P. L. T. Brian, "Gas Absorption Accompanied by an Irreversible Reaction of General Order," A.I.Ch.E. Journal, X (1964), p. 5.

The effect of counterionic diffusion has been estimated by Brian, Baddour, and Matiatos.[10] The authors cite the importance of diffusion of ionic species. The error is considerable if one considers the diffusion of molecular species, when only the cation or anion diffuses and participates in the reaction. The diffusion of reactant ions are retarded by counter diffusion of product ions and by the temporary electric field established by the charged particles. Vinograd and McBain,[11] and Sherwood and Wei[12] reported also on these effects. Brian,[13] et al. have presented an approximate solution which can be used to predict the effective diffusivity of the solute ion. It differs from a true solution by a maximum of 4%.

2. Studies in a Laminar Liquid Jet

Laminar liquid jets have been used for quite some time to measure surface tension effects. One of the earliest publications related to this study on laminar liquid jet in applications to mass transfer was by Scrivens and Pigford.[14] The authors reported on the fluid dynamics

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[10] P. L. T. Brian, R. F. Baddour, and D. C. Matiatos, "An Ionic Penetration Theory for Mass Transfer with Chemical Reaction," A.I.Ch.E. Journal, X (1964), p. 727.

[11] J. R. Vinograd and J. W. McBain, "Diffusion of Electrolytes and of the Ions in Their Mixtures," Journal of the American Chemical Society, LXIII (1941), p. 2008.

[12] T. K. Sherwood and J. C. Wei, "Ion Diffusion in Mass Transfer Between Phases," A.I.Ch.E. Journal, I (1955), p. 522.

[13] Brian, Baddour, and Matiatos, op. cit.

[14] L. E. Scrivens and R. L. Pigford, "On Phase Equilibrium at the Gas-Liquid Interface During Absorption," A.I.Ch.E. Journal, IV (1958), p. 439.

of a jet delivered from a shaped nozzle. The ideal results were compared to some experimental data obtained on CO_2 - H_2O system. Later Raimondi and Toor,[15] and Clarke,[16] showed that a diaphragm (a thin square edged orifice) orifice produced the best velocity profile desired in the liquid jet; i.e. plug flow within a very short distance from the orifice face. Thick orifices provide boundary layer retardation which is not easily estimated. Raimondi and Toor, and Clarke worked with CO_2, with Clarke investigating the absorption of CO_2 in monoethanolamine solutions.

Spalding[17] used the laminar jet to study the absorption of chlorine in water and aqueous sodium hydroxide solutions. Other tests of the penetration theory with chemical reaction have been with short wetted wall columns.

3. Extension to Large Scale Equipment

The theoretical and experimental studies that have been made of absorption with chemical reaction in simple systems will not be of real value for industrial equipment design until manageable ways are found to extend the theories to industrial packed absorbers.[18] Except

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[15] P. Raimondi and H. L. Toor, "Interfacial Resistance in Gas Absorption," A.I.Ch.E. Journal, V (1959), p. 86.

[16] J. K. A. Clarke, "Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times," Industrial and Engineering Chemistry-Fundamentals, III (1964), p. 211.

[17] C. W. Spalding, "Reaction Kinetics in the Absorption of Chlorine into Aqueous Media," A.I.Ch.E. Journal, VIII (1962), p. 685.

[18] Vivian and King, op. cit., p. 453.

for simple cases, the integration of mass transfer expressions over the length of the tower, where the mass transfer is a function of the liquid concentration, is often formidable.

A few papers have touched on the subject, Secor and Southworth[19] have analyzed the case of a second order infinitely fast second order chemical reaction. The authors show how the design may be carried out using integrated equations based on the Hatta film theory. For the simple case a modification of the Colburn N_{OG} versus absorption factor plot can be used in the design. King and Fielding[20] have developed a graphical method for the absorption of nitric oxides in packed columns. The Trambouzes and Piret[21] show the changes in the concentration driving force for a slow irreversible first order chemical reaction.

The scant number of publications indicate the need for design methods which can be extended to commercial scale. The use of electronic computation removes the formidability of many of the intergrations and probably many of the authors cited above have left the individual techniques to the design engineer's development. Levenspiel[22] pointed

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[19] R. M. Secor and R. W. Southworth, "Absorption With an Infinitely Rapid Chemical Reaction in Packed Towers," A. I. Ch. E. Journal, VII (1961), p. 705.

[20] R. W. King and J. C. Fielding, "A Graphical Design Method for Nitric Acid Absorption Towers," Transactions of the Institution of Chemical Engineers, (London), XXXVIII (1960), p. 71.

[21] P. Trambouze, M. T. Trambouze, and E. L. Piret, "Chemical Reaction in Two-Phase Systems," A. I. Ch. E. Journal, VII (1961). p. 138.

[22] O. A. Levenspiel, personal communication, April 28, 1965.

out the need for graphical techniques analogous to those used in stage calculations for distillation and absorption. Thus far most efforts have been thwarted because of the many variables which influence the chemical absorber.

CHAPTER III

THEORY

Absorption involves the transfer of mass from one phase to another. The transport of one substance within a continuous phase is called diffusion. If the transfer is through a phase which is quiescent, it is called molecular diffusion and can be partly described by statistical mechanical theories, which in turn is based on the approximations of molecular motions within the phase. When the phase is in turbulent motion, and the transfer of mass occurs by bulk mixing convective motions, the transport process is called eddy diffusion. This phenomena is the basis for many of the mass transfer relations which are used to describe the system in this study; gas absorption accompanied by chemical reaction. A brief description of each type of diffusion will be used to introduce the use to which the relationships are applied.

1. Fick's Law

Adolf Fick in 1855 founded his diffusion law on experimental observations.[1] These observations were made on the rate of mass transfer through liquid in a vertical tube. A reservoir of the diffusing component was attached to the lower end of the tube, while the upper

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[1] W. Jost, Diffusion in Solids, Liquids, and Gases, (New York: Academic Press, Inc., 1960), p. 439.

end was submerged below the solvent surface. In this way, a concentration gradient was maintained across the diffusion path (see Figure 1).

In the mathematical description of the process for the transfer of A through solvent B, Fick used Fourier's Law of heat conduction as an analog,[2] replacing the coefficient of thermal conduction with a newly defined coefficient of diffusion, D_{AB}.

Fourier's Law[3] is;

$$J_q = - k \, dT/dx \qquad (3\text{-}1)$$

and Fick's Law is;

$$J_A = - D_{AB} \, dC_A/dx \qquad (3\text{-}2)$$

For a binary mixture both systems are similar, and both assume a linear relationship between the flux and the driving force. Equations (3-1) and (3-2) describe the flux in a steady state system.

For the unsteady state case, which is of singular interest in this study, it can be shown[4] that the relationship of concentration to time and distance can be represented as follows:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(D_{AB} \frac{\partial C_A}{\partial x} \right) = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \qquad (3\text{-}3)$$

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[2] H. J. V. Tyrell, Diffusion and Heat Flow in Liquids, (London: Butterworths Inc., 1961), p. vii.

[3] Jost, op. cit.

[4] See Ch. V. Analysis of Research.

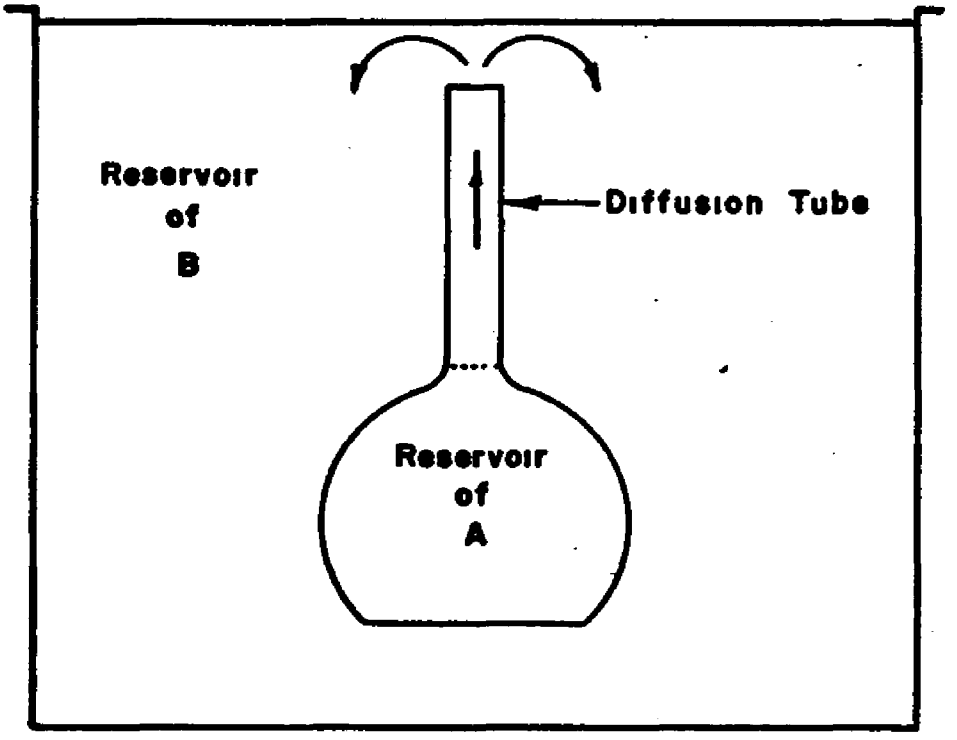

Figure 1, Schematic Diagram of Fick's Diffusion Experiment.

if the diffusion coefficient, D_{AB} is independent of x.[5] Equation (3-3) is called Fick's second law although Fick considered Equation (3-2) to be simply a necessary mathematical step in the derivation of the law of diffusion, Equation (3-3).[6] The analogy between Fourier's Law and Fick's Law also extends to the analytical and numerical solutions which have been obtained for each. Boundary conditions differ for each and have been taken into consideration.

Equation (3-2) is used to characterize molecular diffusion of binary systems with the evaluation of D_{AB}, a parameter called the coefficient of diffusion. Inherent assumptions are;

1) The only driving force for mass flux is the concentration gradient.
2) The mass flux is a linear function of the concentration gradient.
3) The diffusion coefficient is not a function of distance, which is implied by also stating that it is not a function of concentration since concentration is varying with distance.
4) There is no mass transport due to convective currents and bulk mixing.

These conditions are not particularly restrictive for mass transfer of a solute in a liquid for the case of relatively low solubility in which the concentration is not affected very much, so assumption 3) is

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[5]This states that it is primarily independent of the concentration, which is correct in dilute solutions.

[6]Tyrell, op. cit., p. 2.

valid and sound. In laminar flow where all fluid elements are ordered, or in the case of quiescent liquids, condition 4) is also valid. Conditions 1) and 2) are inherent to the model, and while not absolutely correct,[7] the model has been found to be valid in most cases. The above phenomenological equations permit the evaluation of the diffusion coefficient from experimental measurements of fluxes and concentrations. However the coefficient can be theoretically predicted for liquids and gases. The following sections describe the current predictive techniques.

2. Molecular Diffusion

a. Gases

The transport of a substance through a stagnant gas mixture can be predicted to a satisfactory degree of accuracy for certain types of molecules. This results from the advanced state of the kinetic theory of gases. Initially when the kinetic theory of gases was based on the hard sphere model having completely elastic collisions, the rough equations approximated diffusion in only permanent gas mixtures. A significant refinement was the use of Maxwell's velocity distribution law, which allowed the evaluation of a more accurate mean velocity for the gas phase. Initially $\bar{v}$ was calculated to be;

$$\bar{v} = \frac{3RT}{Nm} \qquad (3\text{-}4)$$

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[7] For example the driving force for diffusion may arise out of effects considered in irreversible thermodynamics, Dufour and Soret.

where R/N = k, Boltzman's constant. Assuming Maxwell's distribution it was shown that a better estimate for velocity was;[8]

$$\bar{v} = \frac{8kT}{\pi m} \tag{3-5}$$

The estimate of mean velocity together with the collision diameter of the molecules, allows the calculation of a mean free path. These two parameters are the basis for description of molecular transport, and are used to calculate a coefficient of diffusion.

$$D_{AB} = 1/3\ \lambda_A\ \bar{v}_A \tag{3-6}$$

Equation (3-6) is a rough approximation but it serves as a basis for some reaction kinetics calculations where the inaccuracies of the diffusion model are insignificant compared to other expressions used in the calculations.

The simplifying assumptions of elastic collisions, no intermolecular attraction, and simple collision angles for the interchange of kinetic energy provides a crude model at best. With the evolution of the kinetic theory, the simplifying assumptions could be replaced with more realistic descriptions. The introduction of a factor allowing for angle of deflection provided quite an improvement.

The best equation for estimation of binary diffusion coefficients is;

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[8] Jost, op. cit., p. 415.

$$D_{AB} = \frac{1.858 \times 10^{-3}\, T^{3/2}}{p\, \sigma_{AB}^{2}\, \Omega_D} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}} \qquad (3\text{-}7)$$

where the collision diameter, σ_{AB}, and the collision integral, Ω_D, have to be evaluated for the system. The collision integral is equal to 1.0 for rigid sphere molecules and has to be evaluated numerically for realistic potential functions describing molecular interactions. Hirschfelder,[9] et al. have calculated and tabulated numerical values of the collision integral as a function of the reduced temperature. The emphasis in research continues to be on the development of more realistic intermolecular potential models especially for polar gases.

b. Liquids

The theory of molecular diffusion in liquids is not as advanced as that covering gaseous diffusion. The liquid state has not been categorized quite as well as the gaseous state. The typical substance of average molecular size diffuses through a liquid at a rate which is primarily dependent on the properties of the medium (liquid state). This differs from gaseous diffusion where the rate is determined by the properties of the diffusing solute. The dependency on the liquid properties is exhibited by the narrow range of liquid

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[9] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, (New York: John Wiley and Sons, Inc., 1954).

diffusion coefficients; from 1×10^{-5} to 8×10^{-5} $cm.^2/sec.$ In the absence of a rigorous theory for diffusion in liquids, there are two rough theories which are useful in getting order of magnitude values:[10] the hydrodynamic theory and the Eyring theory.

The hydrodynamic theory is based on a model of quasi-crystalline structure liquids. This is also called the "hole" theory, and assumes that there is a tendency for the adjacent liquid molecules to occupy sites which correspond to those of a regular crystalline lattice. In this structure there are unoccupied sites and imperfections. A foreign particle diffusing through a liquid medium is transported via the "holes" and imperfections. These holes need not be the size of the moving particle provided they permit a certain displacement.[11]

A starting point for the liquid diffusion theories is the Nernst-Einstein Equation[12] which describes the diffusion of a single particle of A through medium B, as:

$$D_{AB} = K\,T\,\frac{U_A}{F_A} \qquad (3\text{-}8)$$

where U_A/F_A is the mobility of the particle A. The relationship between force, F_A, and velocity, U_A may be obtained from viscosity measurements.

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[10] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, (New York: John Wiley and Sons, Inc., 1960).

[11] W. Jost, Diffusion in Solids, Liquids, and Gases, (New York: Academic Press, Inc., 1960), p. 439.

[12] F. Daniels and R. A. Alberty, Physical Chemistry, (New York: John Wiley and Sons, Inc., 1955), p. 650.

After assuming a limiting case of, no tendency for the fluid to stick to the diffusing particle; it can be shown that[13] the diffusion coefficient can be approximated by

$$\frac{D_{AB}\,\mu_A}{k\,T} = \frac{1}{2\pi}\left(\frac{\tilde{N}}{\tilde{V}_A}\right)^{\frac{1}{3}} \tag{3-9}$$

The Eyring rate theory attempts to explain the transport phenomena on the basis of a simple model for the liquid state. The theory gives a relationship very similar to Equation (3-9), but it does not fit the data as well.

One of the best empirical relations is the one by Wilke,[14] based on the Stokes-Einstein equation. The correlation can be expressed by the following analytical expression;

$$D_{AB} = 7.4 \times 10^{-8}\ \frac{(\psi_B\, M_B)^{\frac{1}{2}}\, T}{\mu\, \bar{V}_A^{0.6}} \tag{3-10}$$

where μ = the viscosity of the solution

ψ_B = the association parameter based on the solvent, B.

This relationship applies only for dilute solutions of non-dissociating solutes; and is good within $\pm$ 10 per cent.

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[13] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, (New York: John Wiley and Sons, Inc., 1960), p. 514.

[14] C. R. Wilke, "Estimation of Liquid Diffusion Coefficients," Chemical Engineering Progress, XLV (1949), pp. 218-224.

3. Eddy Diffusion

Substances can be transferred within a phase by the motion of finite parcels of fluid. This process is much more rapid than molecular diffusion and it is in the preferred mode of operation of industrial processes, just as it is in the case of heat transfer. The dispersion generated by turbulence in the fluid is usually measured experimentally and correlated with a few important parameters. Since turbulence has not been completely described mathematically, the eddy diffusion coefficient cannot be predicted from theory. However using an analog of Fick's Law, a parameter called the eddy diffusivity can be evaluated experimentally.

$$J^t = - D^t_{AB} \, d\bar{C}_A/dx \qquad (3\text{-}11)$$

The coefficient is useful if a numerical value of eddy diffusivity is known for the flow regime in question. In chemical engineering technology this is not often evaluated separately but is usually "lumped" in another quantity called the mass transfer coefficient.

4. Interphase Mass Transport

Continuous contacting processes such as absorption, distillation, extraction, drying, and heterogeneous chemical reactions require engineering analysis of complex mass transfer mechanisms. Because of the complexity of the mechanism, the use of empirical correlations to predict the parameters of simple mathematical models have been in use. The achievements of chemical engineering technology attest to

the usefulness of these tools. It is the goal of engineers however to strive for more realistic and definitive mathematical expressions for the description of the rate processes.

a. Two Film Theory

Whitman,[15] and Lewis and Whitman[16] proposed the use of diffusion coefficients per unit area for the description of inter-phase mass transfer. In 1923 there was some uncertainty over the use of a proper driving force to express mass transfer rates. The authors proposed that, in turbulent flow of liquid and gaseous phase, there was a stagnant layer of each phase on either side of the interface. The rate of transfer through these layers were slow and occurred by molecular diffusion. The name given this theory was the two-film theory, although no sharp demarcation lines for the film boundaries were inferred. It was proposed that these coefficients be evaluated experimentally. The relationships which were proposed are:

$$\frac{dW}{Adt} = k_G \ (P_G - P_i) = k_L^o \ (C_i - C_L) \qquad (3\text{-}12)$$

More recent presentations in some textbooks[17] indicate that k_L^o and k_G can be defined as follows:

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[15] W. G. Whitman, "The Two Film Theory of Gas Absorption," Chemical and Metallurgical Engineering, XXIX (1923), p. 146.

[16] W. K. Lewis and W. G. Whitman, "Principles of Gas Absorption," Industrial and Engineering Chemistry, XVI (1924), p. 1215.

[17] T. K. Sherwood and R. L. Pigford, Absorption and Extraction, (2nd Edition; New York: McGraw-Hill, Inc., 1952), pp. 317-339.

$$k_L^o = \frac{D_v}{x} \tag{3-13}$$

$$k_G = \frac{D_v P}{RT \times P_G} \tag{3-14}$$

Because of the impossibility of measuring x, or because it does not exist,[18] the mass transfer coefficients are correlated with physical parameters of the system. Possibly the concept of correlating x arose as the theoretical relationships for predicting the diffusion coefficients became available.

The concept of two films has been quite useful particularly in the form of overall coefficients where the driving force could be expressed as two easily measurable bulk phase concentrations.

$$N/A = K_G (p_G - p^*) \tag{3-15}$$

$$N/A = K_L (c^* - c_L) \tag{3-16}$$

where p^* and c^* are the partial pressures of the solute in equilibrium with a liquid having a bulk concentration of c_L, and the concentration of solution in equilibrium with the bulk solute partial pressure of p_G. Where the gas-liquid system can be described with a linear

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[18] L. Lapidus, Fundamentals of Mass Transfer Processes, Part 1, Separation Processes, ed. R. F. Chapman (New York: Rheinhold Publ. Co., 1961), p. 2.

equilibrium relationship called Henry's Law, $p = mc$, then the two individual mass transfer coefficients can be combined to evaluate the overall coefficients,

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L^o} \tag{3-17}$$

and,

$$\frac{1}{K_L} = \frac{1}{mk_G} + \frac{1}{k_L^o} \tag{3-18}$$

b. Penetration Theory

Because of the difficiencies of the two film theory, it was only natural to inquire into liquid phase diffusion with the possibility of constructing a more realistic model for the mass transfer process. Such a model has been proposed by Higbie,[19] Danckwerts,[20] and Toor and Marchello[21] and is termed the penetration theory.

In a qualitative description, a liquid which flows down a piece of packing has turbulent eddies extending to the surface. Each eddy brings a fresh parcel of fluid to the surface from the bulk fluid.

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[19] R. Higbie, "The Rate of Absorption of a Pure Gas into a Still Liquid during Short Periods of Exposure," A. I. Ch. E. Journal, XXXI (1935), p. 365.

[20] P. V. Danckwerts, "Significance of Liquid Film Coefficients in Gas Absorption," Industrial and Engineering Chemistry, XLIII (1951), p. 1460.

[21] H. L. Toor and J. M. Marchello, "Film-Penetration Model for Mass and Heat Transfer," A. I. Ch. E. Journal, IV (1958), p. 97.

With the assumption of no interfacial resistance, one considers the liquid parcel surface saturated with solute gas. Absorption occurs by molecular diffusion, corresponding to the unsteady state equation presented as Fick's Second Law (Equation (3-3)). The rate of absorption decreases with time until the element of fluid is replaced with another fresh element from the fluid bulk. The overall effect is a continuous replacement of old surface masses with fresh elements. At any one time the entire liquid surface is made up of a series of surfaces with different ages or contact times with the gas phase; the surface is now an unsteady state heterogeneous medium instead of a steady-state homogeneous phase as characterized by the film theory.[22] The real problem associated with this approach is how to characterize the surface age. Higbie[23] proposed that it is the time required for liquid to flow over a packing piece. Danckwerts[24] proposed a time distribution which must be evaluated experimentally and correlated with the flow and packing characteristics of a column.

Fick's Second Law, which is Equation (3-3) above, represents unsteady state one dimensional molecular diffusion into a semi-infinite medium.

$$D_A \frac{\partial^2 C_A}{\partial x^2} = \frac{\partial C_A}{\partial t} \qquad (3\text{-}19)$$

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[22] Lapidus, op. cit.

[23] Higbie, op. cit., p. 365.

[24] Danckwerts, op. cit.

It is shown in Chapter V how this expression can be integrated with proper boundary conditions to represent the average mass flux in a liquid stream.

$$\bar{N}_A = 2\,(C^* - C_o)\sqrt{\frac{D_A}{\pi t'}} \qquad (3\text{-}20)$$

Comparison to Equation (3-12) yields;

$$k_L^o = 2\sqrt{\frac{D_A}{\pi t'}} \qquad (3\text{-}21)$$

The important point to note is that the film theory predicts k_L^o varies linearly with D_A,

$$k_L^o \;\alpha\; D_A \qquad (3\text{-}22)$$

but the penetration theory predicts k_L has a square root dependence on D_A. In a study by Sherwood and Hollaway,[25] the actual behavior in a packed column was shown to be:

$$k_L^o \;\alpha\; \sqrt{D_A}$$

and not D_A to the first power as the film theory predicts.

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[25] T. K. Sherwood and F. A. L. Hollaway, "Performance of Packed Towers - Liquid Film Data for Several Packings," Transactions of the American Institute of Chemical Engineers, XXXVI (1940), p. 39.

5. Interfacial Mass Transfer Accompanied by Chemical Reaction

This study considers the transient transfer of a gaseous solute, CO_2, SO_2, or CH_3SH to an aqueous phase. The methyl mercaptan transfer was studied with various concentrations of sodium hydroxide solutions. The sodium hydroxide is practically completely ionized into Na^+ and OH^- ions in the aqueous phase which are not released (or soluble) in the gaseous phase. The mass transfer process of CH_3SH is accompanied by an irreversible chemical reaction between the transferring specie and the anion, OH^-.

$$CH_3SH_{(\ell)} + OH^-_{(\ell)} \rightarrow CH_3S^-_{(\ell)} + H_2O_{(\ell)} \qquad (3\text{-}23)$$

The reaction is usually written to show the formation of a mercaptide salt, which is also completely ionized in the aqueous phase. Equation (3-23) indicates the mechanism in which we are interested. The product of the chemical reaction CH_3S^- is also considered non-volatile to the gas phase. A schematic drawing in Figure 2 depicts the process indicating the concentration gradients of reactants and products.

The chemical reaction, which was postulated, is assumed to proceed according to the second order kinetic equation:

$$\frac{(\text{moles of } CH_3SH \text{ reacting})}{(\text{time})\ (\text{volume})} = k_F\ [CH_3SH][OH^-] \qquad (3\text{-}24)$$

The reactants, $[CH_3SH]$ and $[OH^-]$ must diffuse toward each other, collide, and exchange a proton, at the rate indicated by k_F, and the products

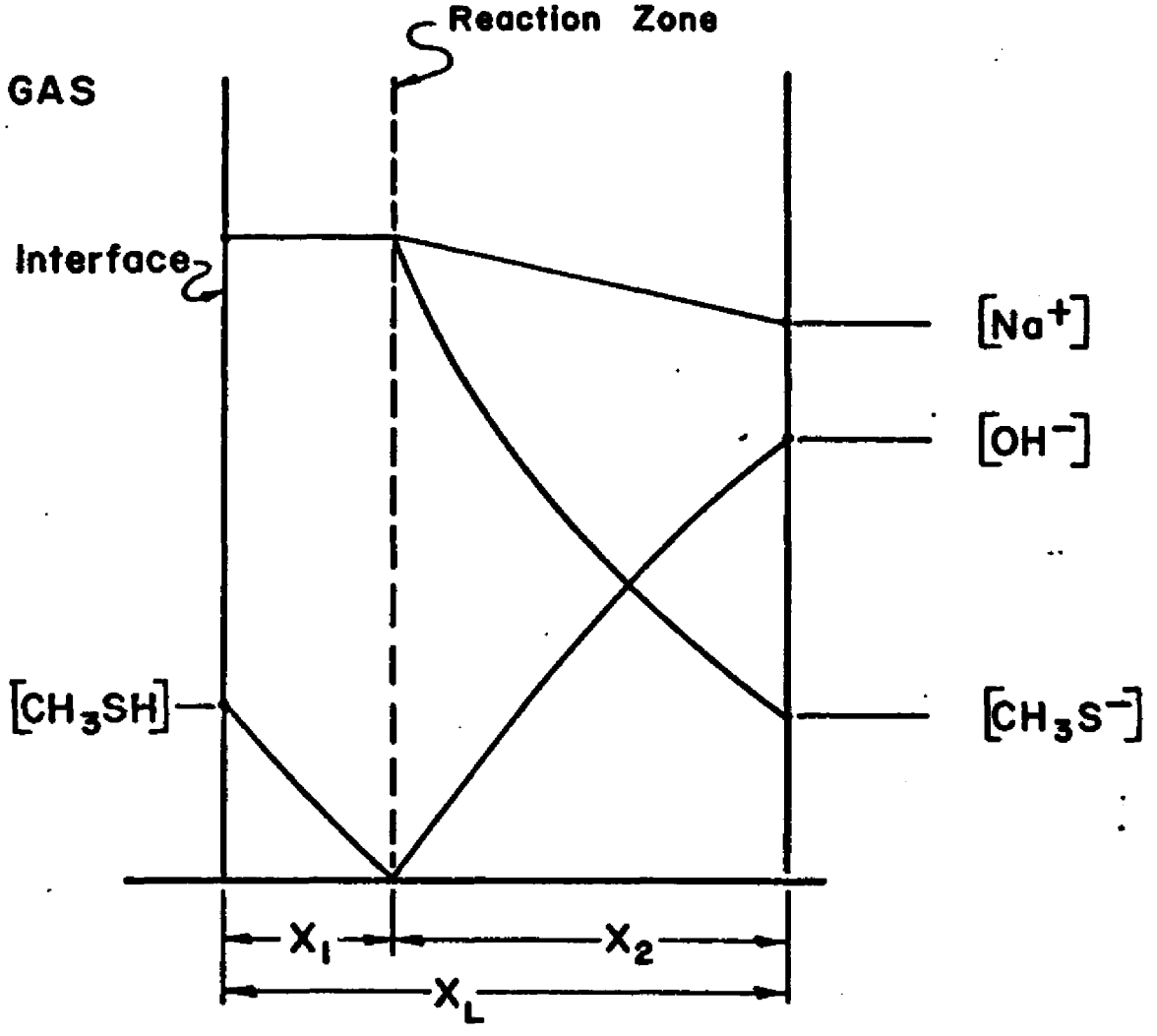

Figure 2, Concentration in Double Film During Absorption of Methyl Mercaptan by Aqueous Sodium Hydroxide.

diffuse back to the bulk liquid since they are not soluble in the gaseous phase. The derivation for this unsteady state case of diffusion with chemical reaction is identical with the penetration theory diffusion case except for the addition of another rate term representing the reaction of $A(CH_3SH)$ and $B(OH^-)$, plus an additional rate equation which must be written on the liquid phase reactant B in order to render the equations soluble. The equations (repeated in Chapter V, Analysis of Research) for component A, is,

$$D_A \frac{\partial^2 c_A}{\partial x^2} - \frac{\partial c_A}{\partial t} = k_F c_A c_B \qquad (3\text{-}25)$$

and for component B, is,

$$D_B \frac{\partial^2 c_B}{\partial x^2} - \frac{\partial c_B}{\partial t} = k_F c_A c_B \qquad (3\text{-}26)$$

where A designates the methyl mercaptan and B is the hydroxyl ion concentration.

The diffusion of component B, the hydroxyl ion, obeys a different law of diffusion that for molecular species, because it is charged and the driving force can be an electrical field instead of strictly concentration gradient. The diffusion coefficient does not represent the slow diffusion of the salt NaOH, but the migration of the OH^- ion. This migration is affected by electrical fields imposed internally by

the counter diffusing CH_3S^-, which moves with a different velocity than the OH^- ion. This will produce a small local deviation from electrical neutrality and result in the establishment of a temporary electric field. The Nernst-Planck Equation[26,27,28,29] describes the diffusion of ions in dilute solutions,

$$N_I = - D_I \frac{\partial [I]}{\partial x} + \frac{F}{RT} E z_I D_I [I] \qquad (3\text{-}27)$$

The second term on the right hand side represents the motion of the ionic species under the influence of an electric field. Several authors[30,31,32,33] have used this equation and approached the problem of solving for an effective diffusion coefficient. Brian[34] showed

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[26] W. Nernst, Zeit, Phys. Chem., (Leipzig) II (1888), p. 613.

[27] Ibid., 4, 129, (1889).

[28] M. Planck, Ann. Physik, XXXIX (1890), p. 161.

[29] Ibid., 40, 561, (1890).

[30] J. R. Vinograd and J. W. McBain, "Diffusion of Electrolytes and of the Ions in Their Mixtures," Journal of the American Chemical Society, LXIII (1941), p. 2008.

[31] T. K. Sherwood and J. C. Wei, "Ion Diffusion in Mass Transfer Between Phases," A.I.Ch.E. Journal, I (1955), p. 522.

[32] T. K. Sherwood and J. M. Ryan, "Mass Transfer to a Turbulent Fluid With and Without Chemical Reaction," Chemical Engineering Science, XI (1959), p. 81.

[33] P. L. T. Brian, R. F. Baddour, and D. C. Matiatos, "An Ionic Penetration Theory for Mass Transfer with Chemical Reaction," A.I.Ch.E. Journal, X (1964), p. 727.

[34] Ibid., Equation 18, p. 731.

how an approximate solution could be derived for the determination of an effective diffusivity:

$$r_{eff} \equiv \frac{D_B^-}{D_A} \equiv \frac{2\ R_A}{1 + \sqrt{B\ (R_A/R_P - 1) + 1}} \tag{3-28}$$

For hydroxyl ions and methyl mercaptan the expanded equation (for the ratios) becomes:

$$r_{eff} = \frac{2\ (D_{OH^-}/D_{CH_3SH})}{1 + \sqrt{\frac{D_{OH^-}/D_{CH_3SH}}{D_{CH_3S^-}/D_{CH_3SH}}}} \tag{3-29}$$

since B = 1, for a monovalent anion, and the R's are ratios of the diffusion coefficients. Equation (3-28) was used to calculate the effective diffusivity of the hydroxyl ion. The details are given in Appendix A.

The solution of Equation (3-25) and (3-26) are obtained by numerical analysis, after normalization by substituting the following dimensionless variables.

$$a = C_A/C_{A_i}$$

$$b = C_B/C_{B_o}$$

$$z = (\sqrt{k_F\ C_{B_o}/D_A})\ x$$

$$\theta = k_F B_o t$$

$$r = D_A/D_B$$

$$q = C_{B_o}/C_{A_i}$$

The normalized equations are:

$$\frac{\partial^2 a}{\partial z^2} - \frac{\partial a}{\partial \theta} = ab \qquad (3\text{-}29)$$

$$rq \frac{\partial^2 b}{\partial z^2} - q \frac{\partial b}{\partial \theta} = ab \qquad (3\text{-}30)$$

at a specific r and q, the equations are solved for a and b as a function of θ and Z. The parameter r is evaluated with Equation (3-28), and q is the ratio of the hydroxyl ion at the beginning of the exposure, and the equilibrium concentration of methyl mercaptan at the interface. The details of the solution are given in Chapter V. Once a and b are determined as a function of θ and z the effect of chemical reaction on the mass transfer can be determined. An enhancement factor Φ has been defined which relates the absorption coefficient with reaction to the absorption in the absence of reaction, i.e. physical absorption. Considering a material balance rate equation for consumption of a and b by the reaction and ratioing this expression to the penetration theory for physical absorption, an expression for evaluating Φ can be obtained. (The details of the derivation is in Chapter V).

$$\Phi = \frac{\pi}{4\theta} \int_o^\infty [a + q\ (1 - b)]\ dz \qquad (3\text{-}29)$$

The normalized variable θ ($\theta = k_F^{\sim} C_{B_o} t$), which has the contact time, t, in its definition, is eliminated by substituting for it from the penetration theory solution

$$k_L^o = 2\sqrt{\frac{D_A}{\pi t}} \qquad (3\text{-}21)$$

$$t = \frac{4 D_A}{\pi k_L^{o2}} \qquad (3\text{-}30)$$

and

$$\theta \equiv k_F C_{B_o} t \qquad (3\text{-}31)$$

Substituting for t in Equation (3-31), the result is

$$\theta \equiv k_F C_{B_o} t = \frac{4}{\pi} \left[\frac{k_F C_{B_o} D_A}{k_L^{o2}} \right] \equiv \frac{4}{\pi} [M] \qquad (3\text{-}32)$$

Equation (3-29) becomes,

$$\Phi = \frac{\pi}{4\sqrt{M}} \int_0^{\infty} [a + q\ (1 - b)]\ dz$$

The more general variable M can be interpreted as a measure of how rapid the chemical reaction is, relative to physical absorption in an absorber with the physical absorption coefficient, k_L^o. A typical solution for second order irreversible reaction is depicted in Figure 3. At the asymptotic sections of high M, the reaction is so fast the absorption process has no resistance in the liquid phase due to chemical reaction.

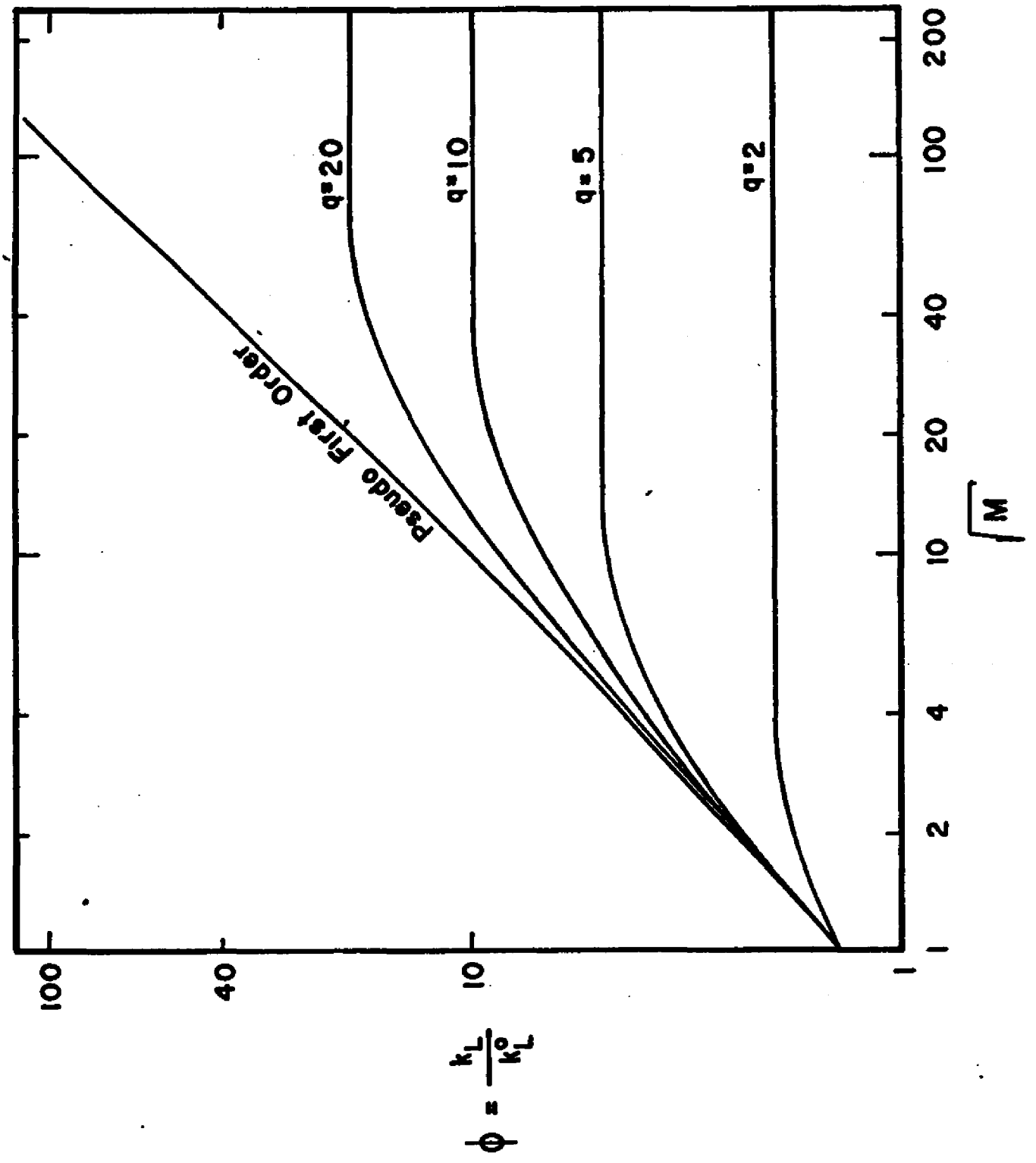

Figure 3, Theoretical Solution for Penetration Theory Accompanied by Irreversible Second Order Chemical Reaction. (after Brian, et al, 1961)[4]

CHAPTER IV

EXPERIMENTAL WORK

1. Laminar Liquid Jet

A versatile gas absorption device, called a laminar liquid jet, was fabricated to study the diffusion coefficients, mass transfer coefficients, and the kinetics of absorption with chemical reaction. Himmelblau[1] reports that the device is suitable for measuring diffusion coefficients with an accuracy of ± 1%. Photographs and an engineering drawing show the details of construction of the assembled apparatus. Figures 4, 5, 6A, and 6B. One of the important parts of the jet is the orifice through which the absorption liquid discharges. Thin sharp edged orifices produces the minimum amount of boundary layer retardation. In order to assure a permanent diameter calibration by the elimination of corrosion, the orifice was machined out of 0.003 in. platinum sheet. A 0.0561 inch hole was drilled in the orifice plates which were mounted in compression between brass blanks. A smooth sharp edged hole resulted from the precision drilling. Figure 6A and 6B.

The orifice was mounted at the end of a piece of precision Pyrex glasstubing, ground flat at the end. The apparatus is equipped with

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[1] D. M. Himmelblau, "Diffusion of Dissolved Gases in Liquids," Chemical Reviews, LXIV (1964), pp. 527-550.

a 2 inch diameter glass tubular absorption chamber, 14.75 inches long, and jacketed with a concentric Plexiglas shell to provide an annulus for circulating water. Figure 4. Care was taken in the machining of the parts to assure precise perpendicularity and alignment of orifice and receiver. Alignment screws were provided to adjust a floating head supporting the orifice and tube; and to compensate for metallic expansion and inaccuracies in the glass tube. The receiver was fashioned by fusing a short piece of 1.85 mm. I.D. capillary glass tube and having an internal diameter only slightly larger than the liquid jet. Figure 5. This design minimized end effects by the elimination of entrained gas and allowed for precise level control in the receiver with a fine needle valve, a 1/4", Whitey, 22S4. The liquid in the receiver was controlled to within 0.05 mm. of the overflow point at the top. The jet length was read at the top of controlled liquid level.

The equipment in contact with the gas and absorbing liquid was fabricated out of glass, Teflon, and stainless steel (316). The floating head was sealed with a fluorocarbon elastomer ring ("O"-ring) under compression. The gas inlet and outlet ports were at opposite ends of the cell designed to provide for positive gas flushing of the absorption chamber.

The temperature of the cell and absorbant was controlled with a thermoelectric, circulating constant temperature bath, marketed by Scientific Apparatus, Inc. The circulating water was controlled within $\pm$ 0.01^{o}C, and the room temperature controlled within $\pm$ 2^{o}C of 25^{o}C. Figure 7.

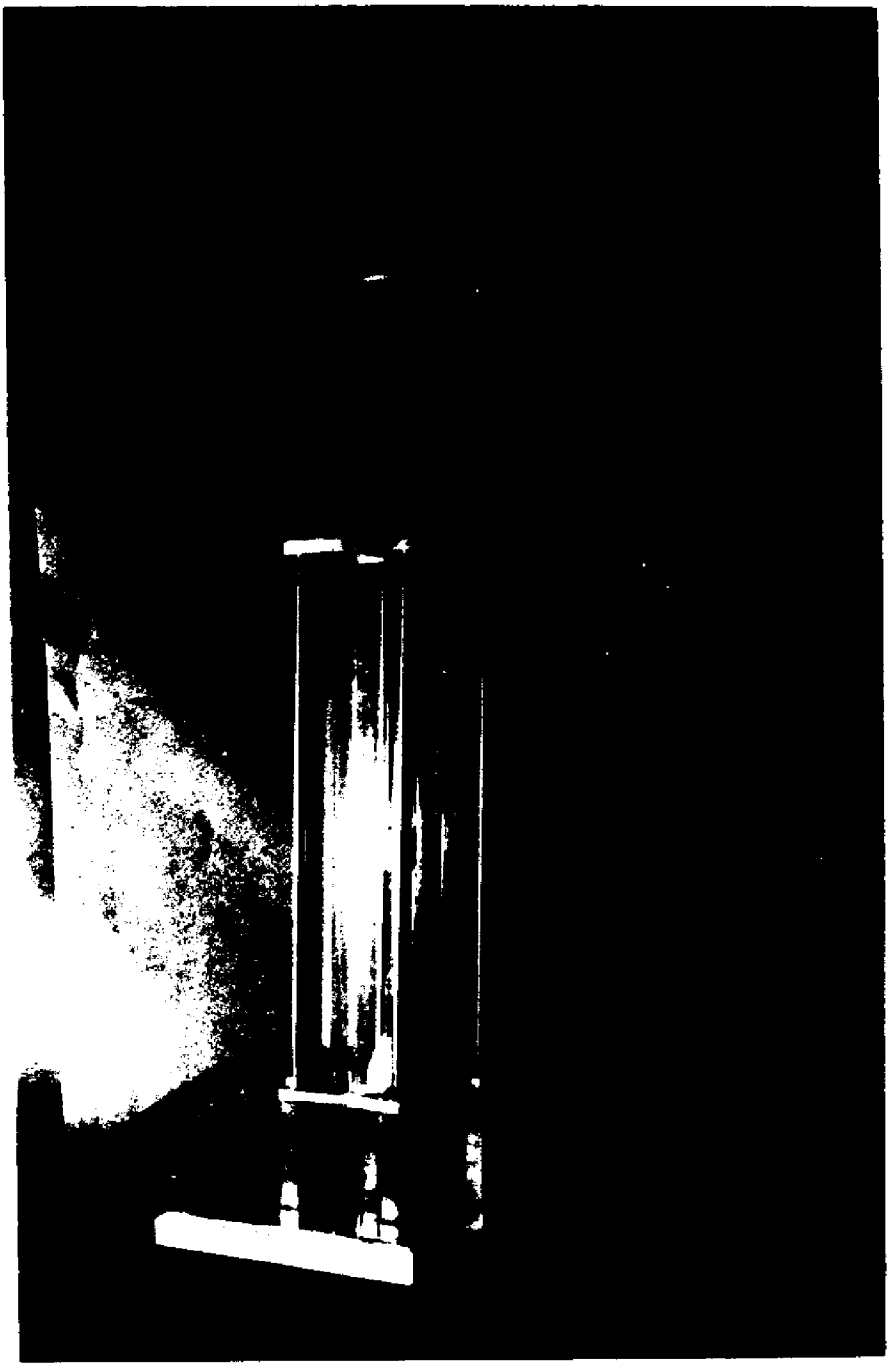

FIGURE 4, PHOTOGRAPH OF LAMINAR JET ABSORPTION APPARATUS

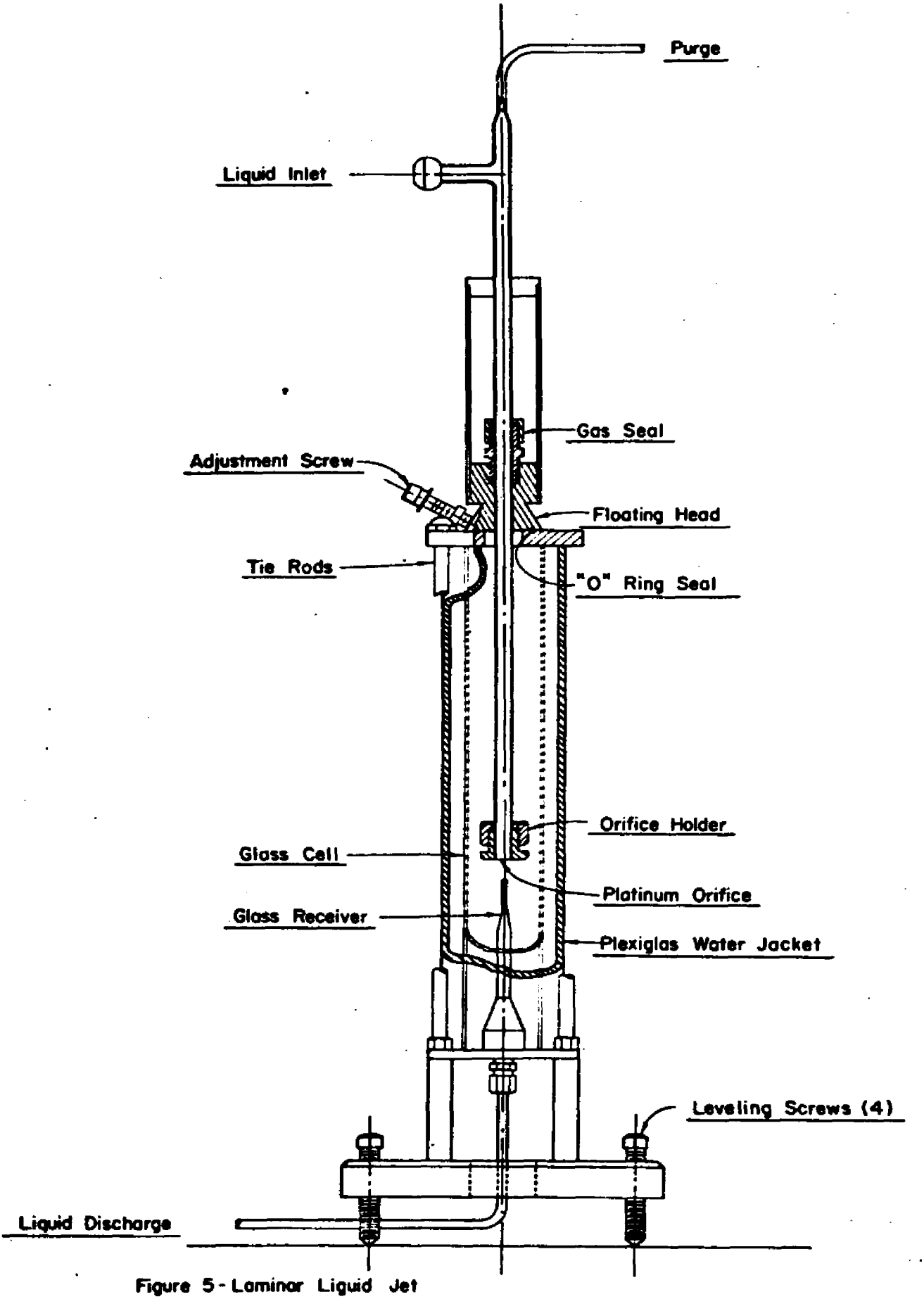

Figure 5 - Laminar Liquid Jet

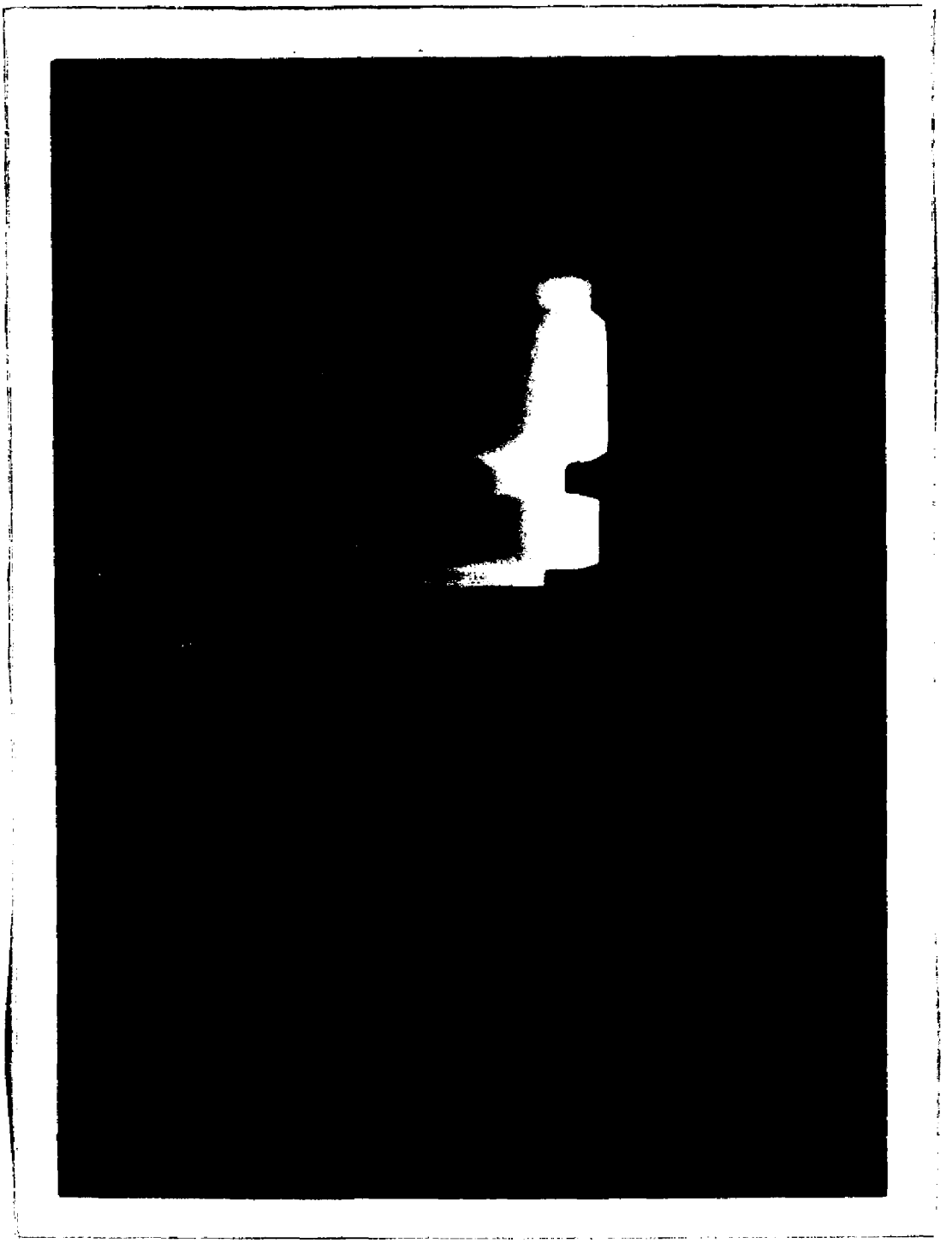

FIGURE 6A, PHOTOGRAPH OF LIQUID JET

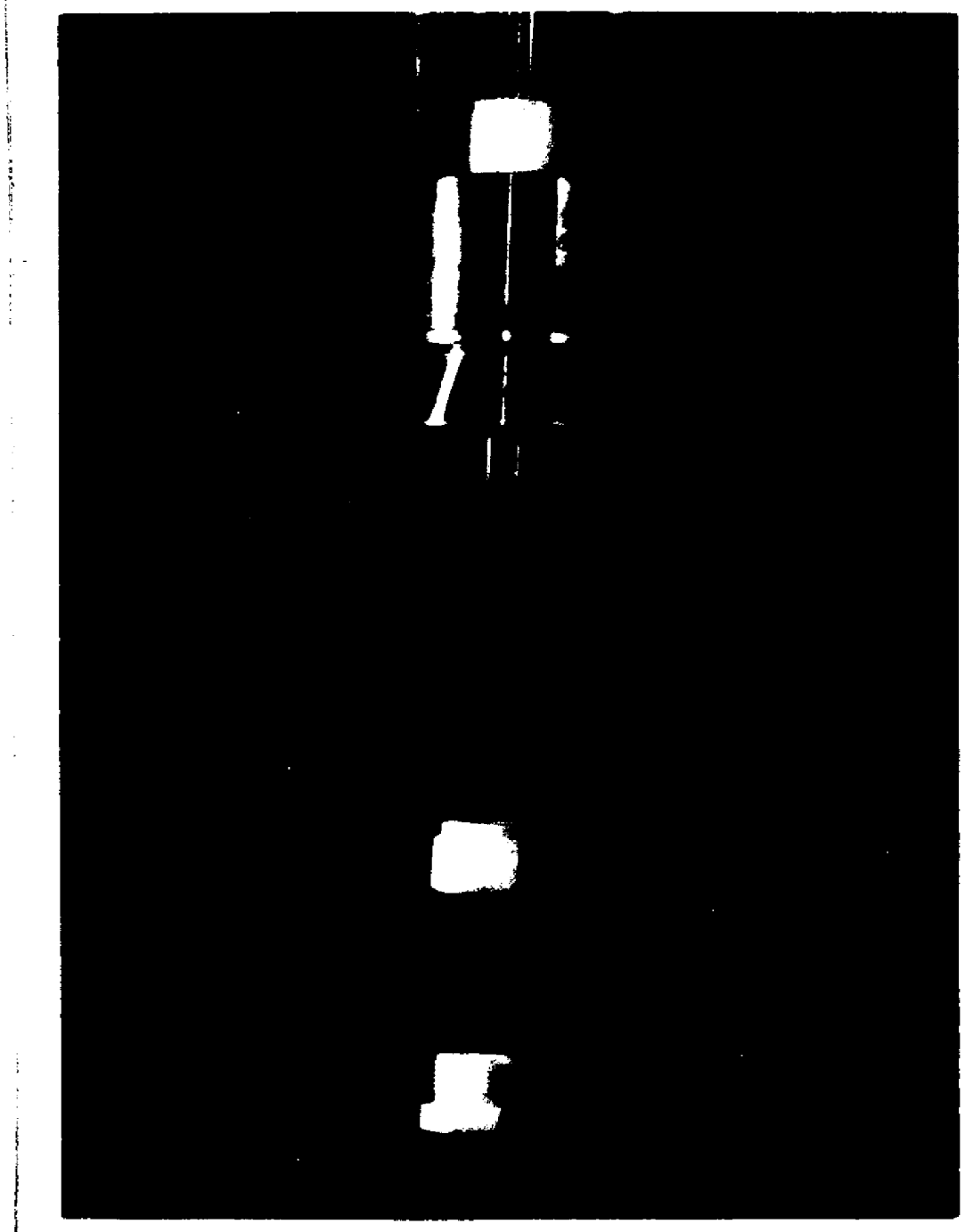

FIGURE 6B, PHOTOGRAPH OF ORIFICE ASSEMBLY

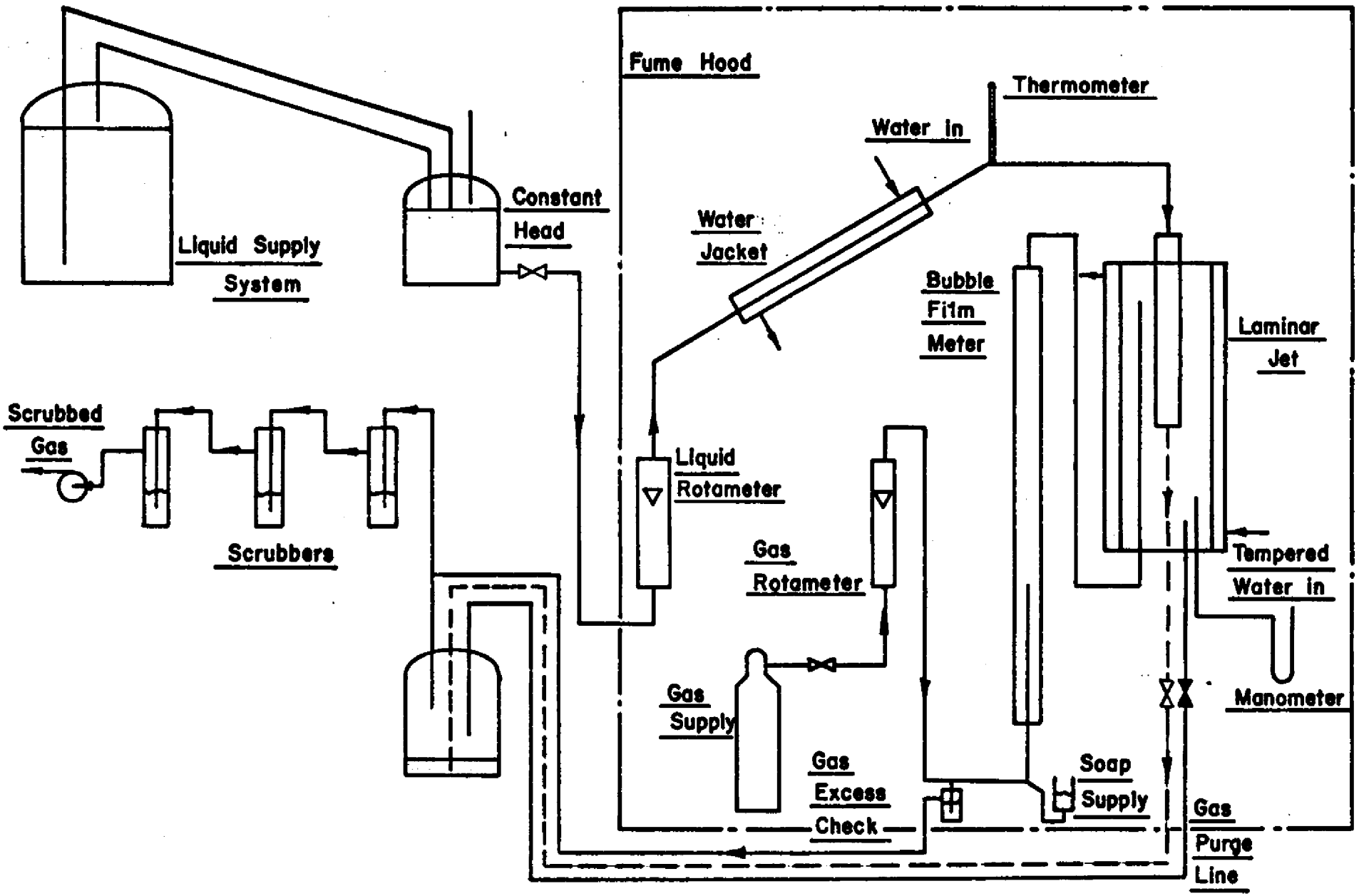

Figure 7 - Schematic Flow Diagram of Absorption Apparatus

The level of the liquid feeding the rotameters was maintained within ± 0.5% with an automatic syphon level controller. The liquid to the orifice was metered with a calibrated Fisher and Porter Flowrator rotameter, No. 3F-3/8-25-5, with a glass float, Type CD-38.

The laminar jet was mounted on a table-type suspension system built from 4" x 4" and 2" x 6" wooden members. The table was anchored to the concrete floor independent of the laboratory bench top, where the ventilation blowers and circulation pumps were mounted. This vibration-free mounting of the absorption cell provided satisfactory jet stability without any ripples as determined by microscopic examination.

The gas absorption rates into the liquid jet was metered with a bubble film flowmeter. The bubble film flowmeter was fabricated out of a standard 50 ml. liquid burette by reshaping the inlet to allow the introduction of a single soap film; and by building a bubble breaker and liquid soap return line from the top outlet. The used soap solution was recycled to the bubble meter inlet. A positive gas purge under slight pressure was maintained at the inlet of the film meter, by metering excess gas through a dip tube submerged 1/16 inch below a water interface. This procedure, in conjunction with pressure readings in the cell chamber assured an adequate gas supply at atmospheric pressure to the gas chamber. This technique was tested by analyzing the liquid effluent during the SO_2 calibration runs. The technique was found to be more precise and as accurate as the iodometric titration analysis of sulfur dioxide in water. The rate of absorption was measured by timing displacement of gas as indicated by the rise of a soap bubble film in the gas burette.

2. Diameter Measurements

Review of the literature indicated that the thin plate orifice would produce a jet of nearly constant diameter; with the maximum diameter variation occurring in the first 0.1 cm. below the orifice. The diameter of the laminar liquid jet was measured with a Gaertner travelling microscope at three liquid flows, at two angles, and at various points along the jet length. The diameter measurements at right angles indicated the jet was circular within the accuracy of the microscope which was ± 0.1%. Diameter measurements indicated that the jet was near ideal and could be represented by the Equation (4-1) at approximately one centimeter[2] below the orifice.

$$\frac{D}{D_o} = \left(1 + \frac{\pi^2 g D_o^4 y}{8 q'^2}\right)^{-1/4} \qquad (4\text{-}1)$$

where D_o = the initial diameter of the jet, cm.

g = gravitational acceleration, cm./sec.^{2}

q' = flow rate, cm.^{3}/sec.

y = jet length, cm.

Figure 8 shows the curvature of the jet to scale. The contraction of an inviscid jet is shown as a comparison. The diameter is very nearly constant along most of the jet length and the use of a mean diameter for a jet of certain length and flowrate is hereby justified.

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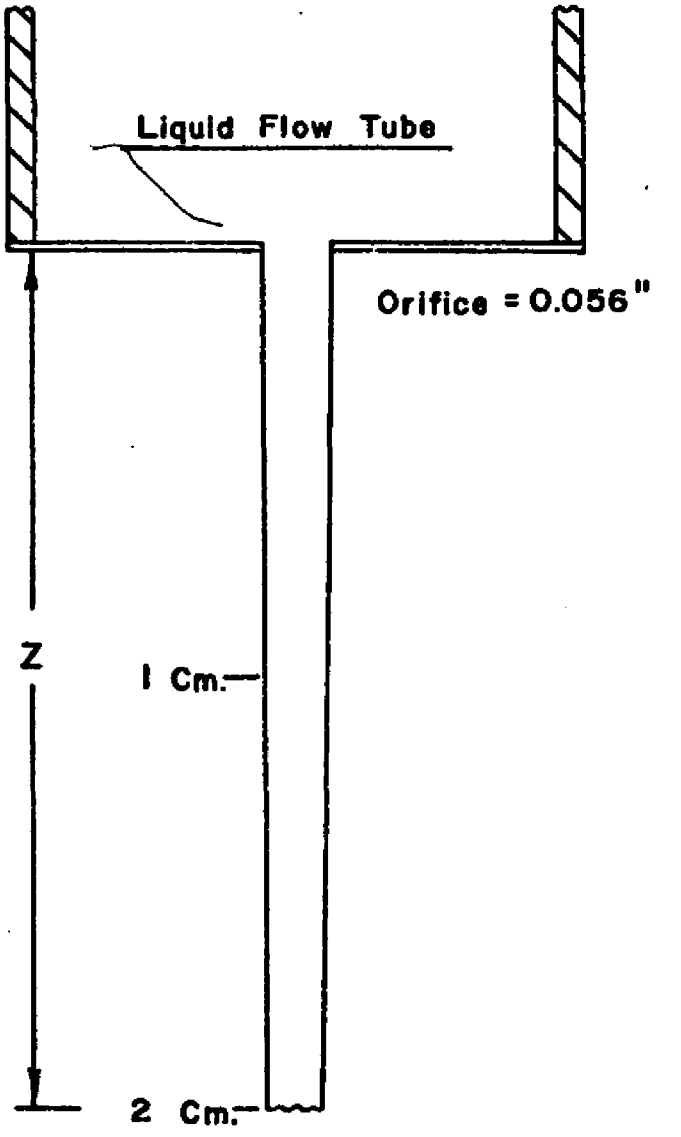
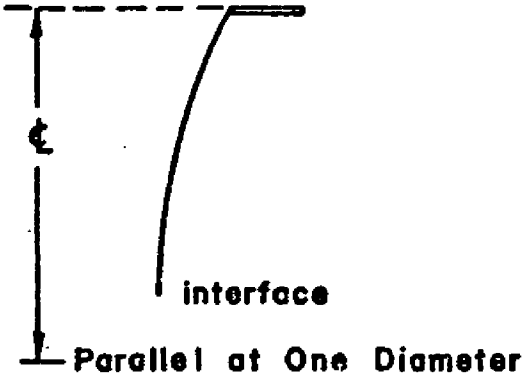
[2] L. E. Scrivens and R. L. Pigford, "On Phase Equilibrium at the Gas-Liquid Interface During Absorption," A.I.Ch.E. Journal, IV (1958), p. 439.



(A) Free Jet Diameter (to scale)



(B) Curvature of Inviscid Liq. Jet

Figure 8, Curvature of Liquid Jet to Scale

3. Test Materials

The compressed gases which were used in the studies are carbon dioxide, sulfur dioxide, and methyl mercaptan. These gases were obtained from the Matheson Company with the following certified purity:

Carbon Dioxide	99.99%
Sulfur Dioxide	99.9 %
Methyl Mercaptan	99.0 %

The water used in the absorption studies was distilled in a Barnstead Still with a modification for condensation under a positive steam purge. As a precautionary measure the warm water was subjected to low vacuum while it cooled, to remove any dissolved gases which might have been absorbed during distillation.

Sodium hydroxide, used in making up absorbing solutions, was a technical grade. The concentration of the solutions was determined by volumetric analysis using HCl as the titrant.

4. Calibration Procedures

The laminar liquid jet was first tested on the absorption of SO_2 in water as one of the first steps in the calibration of the equipment. Thermal stability was established in the absorption apparatus, after about one hour of circulating the tempered water. The gas absorption chamber was flushed for 15 minutes with 100 cc./minute of sulfur dioxide. The liquid jet was started initially with no liquid level in the receiver. All air bubbles had previously been purged from

the receiver and liquid system. With the gas continuously flushing the absorption cell, the soap film gas meter was readied by allowing a few bubbles to pass through the gas burette. With a liquid flow rate set and the jet centered over the receiver, the level in the receiver was brought up gradually by closing the needle valve slowly, being careful not to spill any liquid over the chamber. The gas chamber was sealed by closing off the purge outlet; and the gas flow was lowered while maintaining a slight positive purge past the meter inlet. As the gas was absorbed by the liquid, the volumetric uptake of the gas was timed by noting the rate of movement of the bubble film in the gas burette. Additional soap films could be placed in the gas burette without interrupting the gas flow, as the older films broke or passed into the soap recycle chamber. The length of the jet from the orifice to the receiver was measured with a Gaertner cathetometer (a vertically travelling microscope) which will detect distances within ± .05 mm.

The contact time was varied by changing the liquid flow rate and jet length. The jet length could be changed by shutting off the apparatus, releasing the compression fitting on the receiver, moving the receiver vertically, and then tightening the compression fitting. The procedure for starting up was followed again to get a series of observations at this new jet length.

The gas burette was calibrated by collecting samples of liquid effluent and titrating for SO_2. The liquid flowed through an automatic 10 ml. pipette and discharged to a flask containing a known equivalent weight of iodine. The iodine was back titrated with sodium thiosulfate as in standard iodometric titration procedures.

All excess gas from flushing and purging sequences had to be collected, scrubbed, and vented outside. Sulfur dioxide and later methyl mercaptan made the use of a strong oxidant ($KMnO_4$) in the gas scrubbers imperative. Positive venting lines were connected to the cell flushing outlet, the gas burette purge, and the liquid receiver vessel. The gas was drawn through a series of three $KMnO_4$ gas washing bottles and pumped to an external building vent with a high volume carbon vane vacuum pump.

The entire technique and apparatus were tested by obtaining measurements on the system CO_2 - H_2O at 25°C. This system has been thoroughly studied and accurate data on the diffusion coefficient of carbon dioxide is available. The experimental procedure was similar to the one described above for sulfur dioxide, with the exception of the liquid analysis. The absorption of the CO_2 in water was so low at the normal contact times; that normal titrimetric procedures were too insensitive. The water used in this study remained sealed from the atmosphere throughout the absorption runs to prevent absorption of ambient CO_2. The calibration showed the technique and the apparatus fundamentally sound. The results are discussed in Chapters V and VI.

5. Experimental Procedures

The experimental procedures for absorption with chemical reaction are similar to the one used on calibration studies. The aqueous solutions of sodium hydroxide were mixed and allowed to stand for an hour or more. Multiple samples of solution were withdrawn from the vessel and titrated for NaOH. The solutions were subjected to a vacuum of 29 in. Hg. for

another hour to remove traces of dissolved gases which might have interferred with the absorption study. Tempered water was circulated through absorption cell and solution heat exchanger until thermal stability was reached. The gas burette and cell were flushed with pure gas for 15 minutes. The jet was adjusted to a predetermined length and the liquid flow to the orifice adjusted. When all condition were satisfactory the chamber was sealed and the gas absorption rate timed on the bubble film flow meter. Several determinations were made at a liquid flow rate and jet length until the precision was satisfactory. The liquid flow rate was changed holding the jet length constant and additional determinations made at this point. The apparatus was shut off, the jet length changed, the cell purged, and the start up procedure repeated over again. Temperature, barometric pressure, cell pressure, liquid rotameter reading, jet length, and the determination of absorption rate were the raw data recorded.

A change in liquid concentration required an extensive flushing of all, liquid lines, orifice, and receiver. The restart procedure as described above was followed for each jet length at a sodium hydroxide concentration.

CHAPTER V

ANALYSIS OF RESEARCH

The analysis of the data involves the use of a fluid mechanic model, solutions to the penetration theory, and a packed absorber model which are too specialized to include in Chapter III, The Theory, but important enough to be included in a separate chapter apart from the Appendix. The following sections describe the details of the analysis of research.

1. Fluid Mechanics

One of the conditions on which the penetration theory is based on the non-turbulent condition of the liquid into which the solute diffuses. This condition rules out bulk mixing and eddy diffusion. The laminar jet used a commonly observed phenomenon; that is, a liquid stream in free fall accelerates with negligible momentum interchange across the interface with the gas phase. In free fall each fluid particle is affected to the same degree by gravitational force. Since the system is isolated, there is no mixing due to momentum exchange and the velocity profile is flat. Figure 9 shows how the velocity profile develops. For a jet discharged from a thin orifice the boundary layer retardation caused by contact with the orifice walls

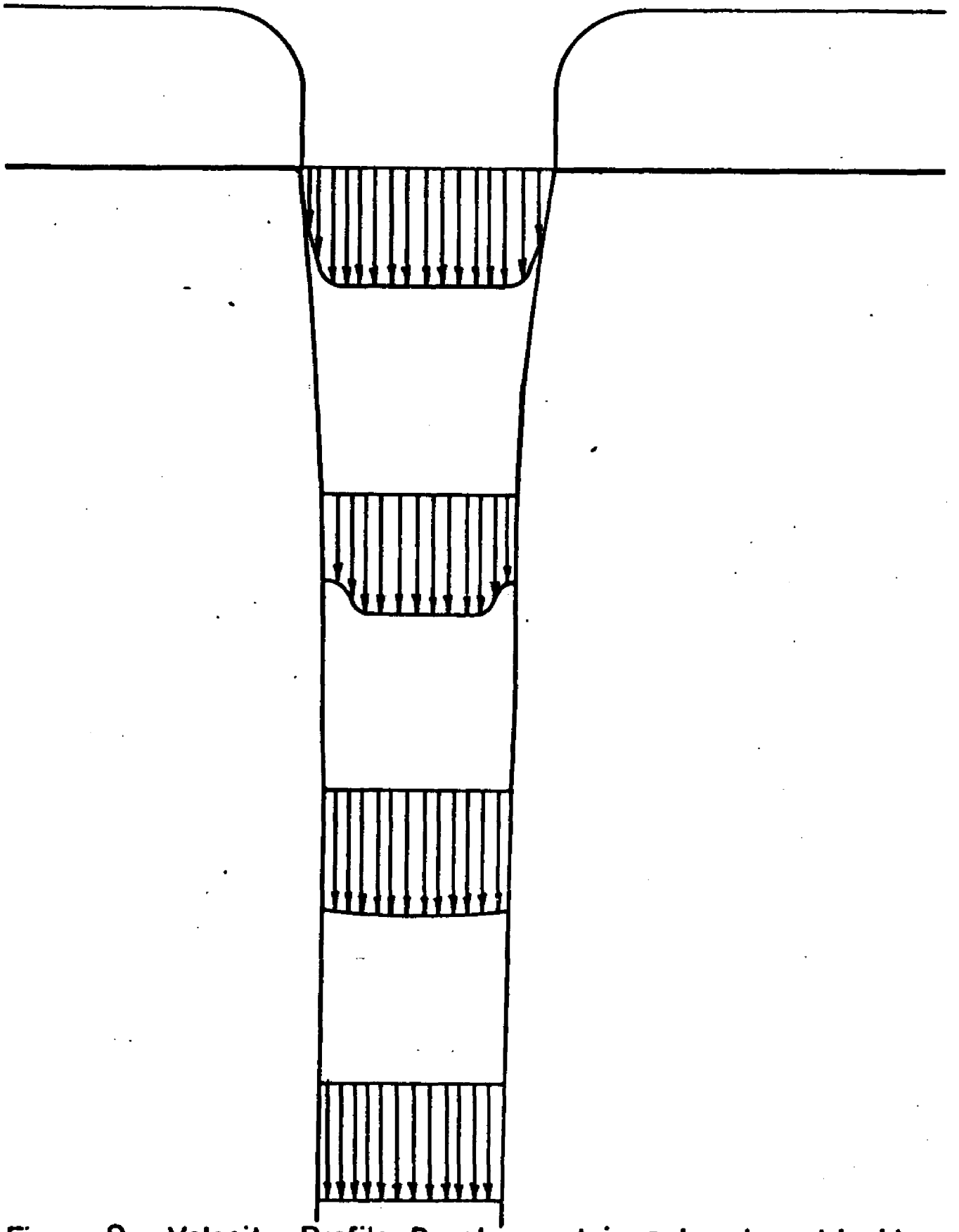


Figure 9, Velocity Profile Development in a Laminar Liquid Jet.

is minimal and the velocity profile is flat at 0.1 cm.[1] beyond the orifice. The assumption of a flat velocity profile or rod-like flow is justified. The variation in diameter is very small after the initial contraction. Figure 8 shows the measured contraction to scale. The small variation in diameter is caused by gravitational acceleration and the velocity of the jet can be represented by the following equation.

$$u^2 = u_o^2 + 2g_L\, y \tag{5-1}$$

From this expression and the equation of continuity it follows that:

$$\frac{D}{D_o} = \left(1 + \frac{\pi^2\, g_L\, D_o\, y}{8q^2}\right)^{-1/4} \tag{5-2}$$

The agreement between observed diameters and that predicted by Equation (5-2) is quite good in the sections where the boundary layer effects have dissapated. The diameters were measured at three flow rates and compared with the diameters predicted by Equation (5-2) in Figure 10, 11, and 12.

2. Penetration Theory

In the penetration theory model, the liquid flows in laminar flow down a piece of packing with a flat velocity profile. Mass transfer

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[1] J. K. A. Clarke, "Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times," Industrial and Engineering Chemistry - Fundamentals, III (1964), p. 211.

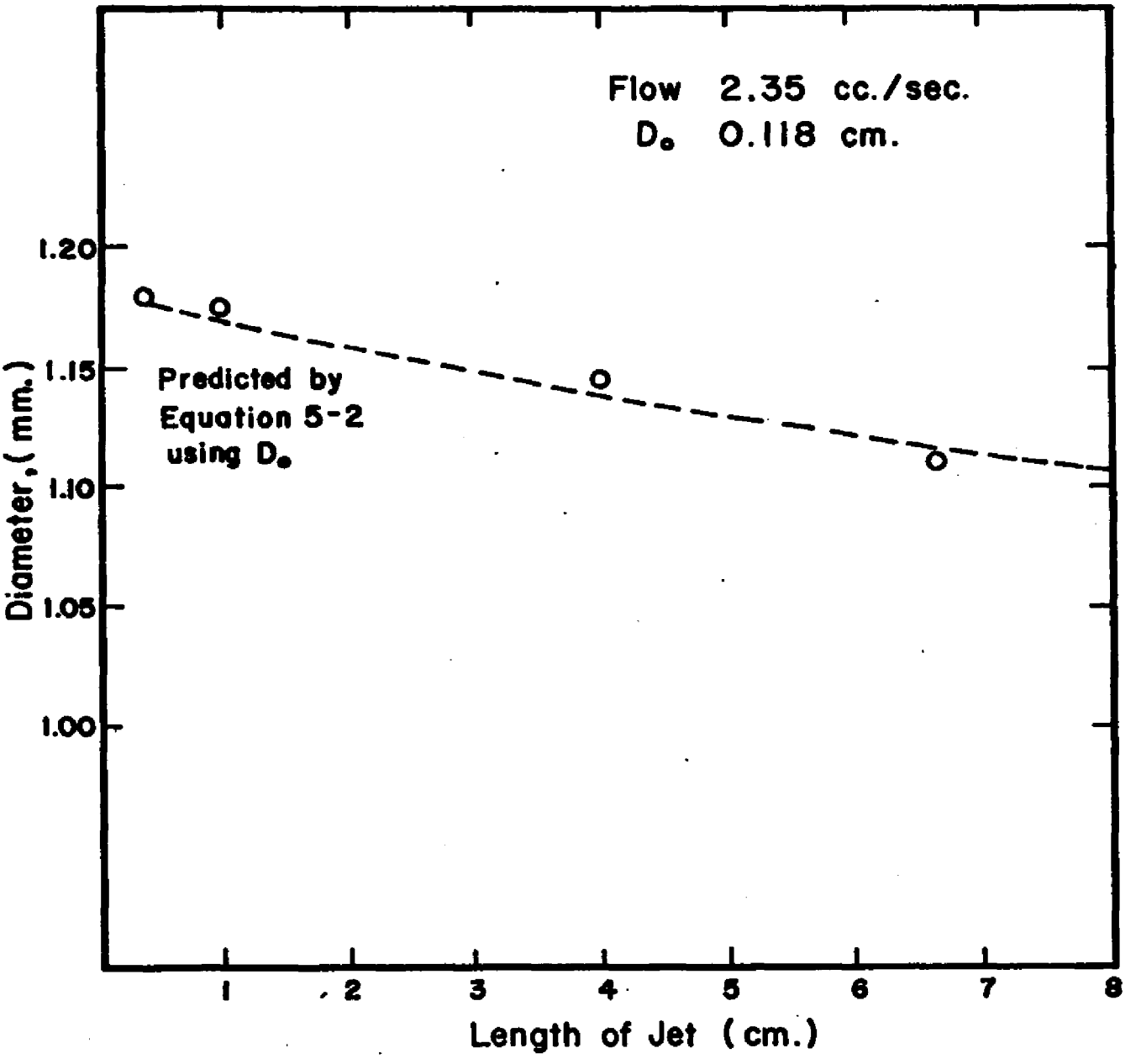

Figure 10, Diameter of Laminar Liquid Jet

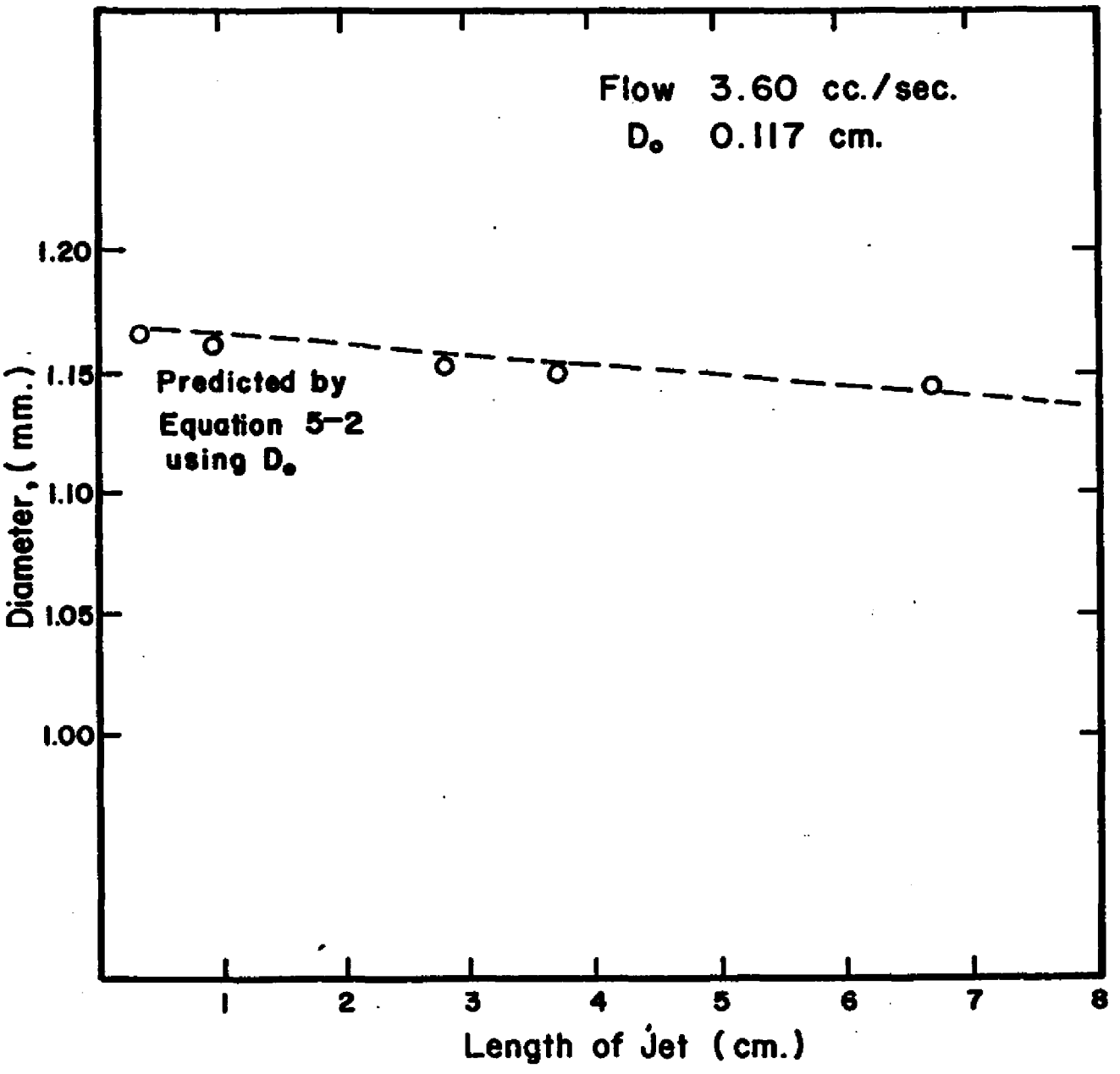

Figure 11, Diameter of Laminar Liquid Jet

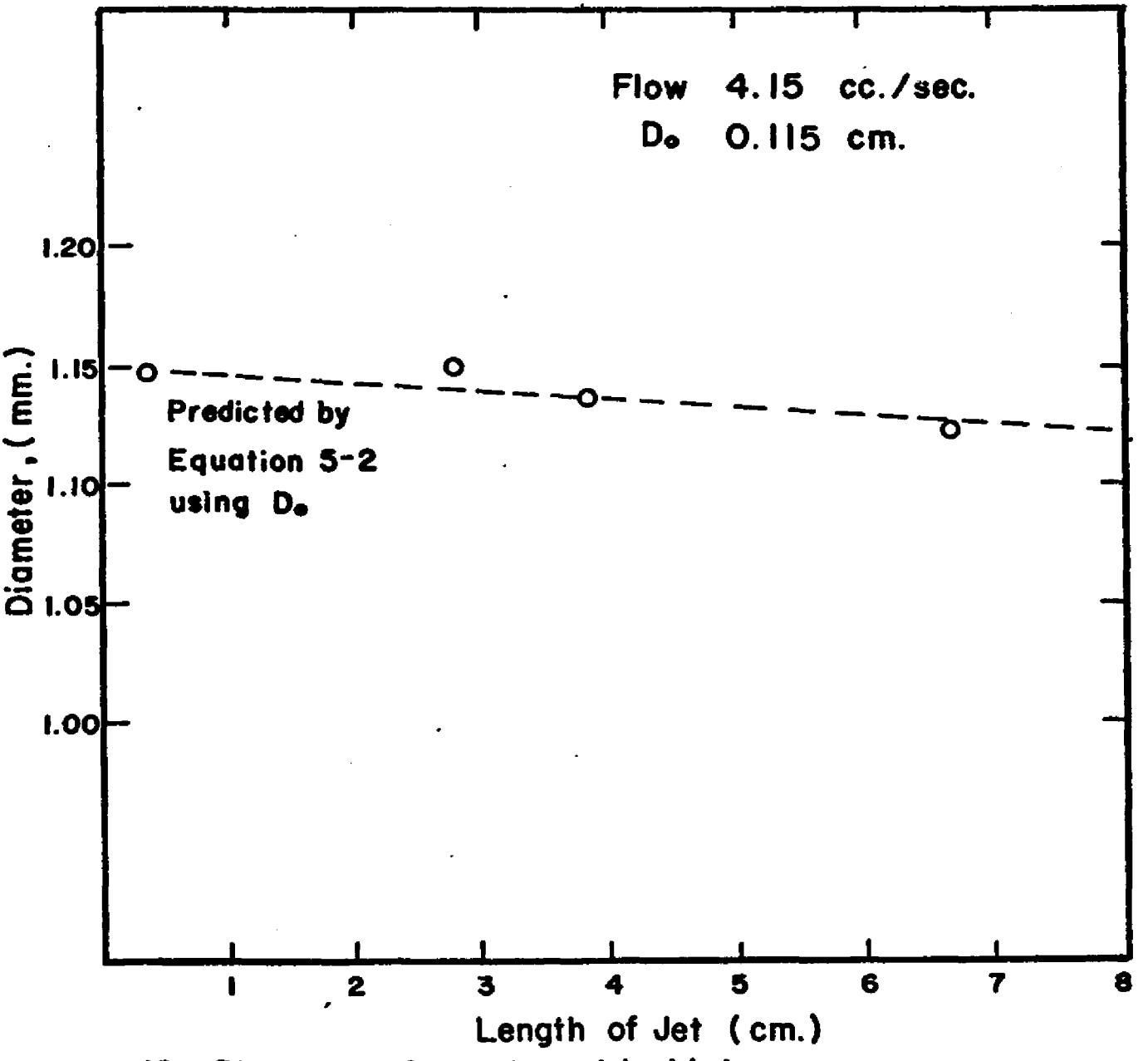

Figure 12, Diameter of Laminar Liquid Jet

takes place by molecular diffusion for a certain contact time. The contact times are so short that the gas does not penetrate deeply into the liquid, and the liquid depth is assumed infinite. For the case of diffusion into a cylinder of fluid, the liquid penetration depth is also too shallow to be affected by the curvature of the cylinder. When the conditions cited in Chapter III are met, Fick's Second Law can be solved for the unsteady state case to express the mass transfer to a slug of liquid during a short exposure. Figure 13 shows the coordinates of a system in the derivation of Fick's Law. A control element δx, of unit width, is chosen; bounded by the coordinate x, and $x + \delta x$. Diffusion into the element is a function of the linear concentration gradient, dC/dx, which is in essence Fick's First Law. Following the laws of conservation of mass, the mathematical expression for rate of transfer of A can be written:

$$\text{Input} \quad - \quad \text{Output} \quad = \quad \text{Accumulation}$$

$$D_A \frac{\partial C_A}{\partial x} - \left[D_A \frac{\partial C_A}{\partial x} + \frac{\partial}{\partial x}\left(D_A \frac{\partial C_A}{\partial x}\right) \delta x\right] = \frac{\partial}{\partial t}\left(C_A \delta x\right) \qquad (5\text{-}3)$$

That is, the rate of mass transfer of A <u>input</u>, minus the rate of mass transfer of A <u>output</u>, is equal to the accumulation of A in the control element. The rate of mass transfer out is equal to the rate in plus the rate of change of the flux over the element δx. Taking the diffusion coefficient as constant, which it is for the case of low concentrations, the equation becomes:

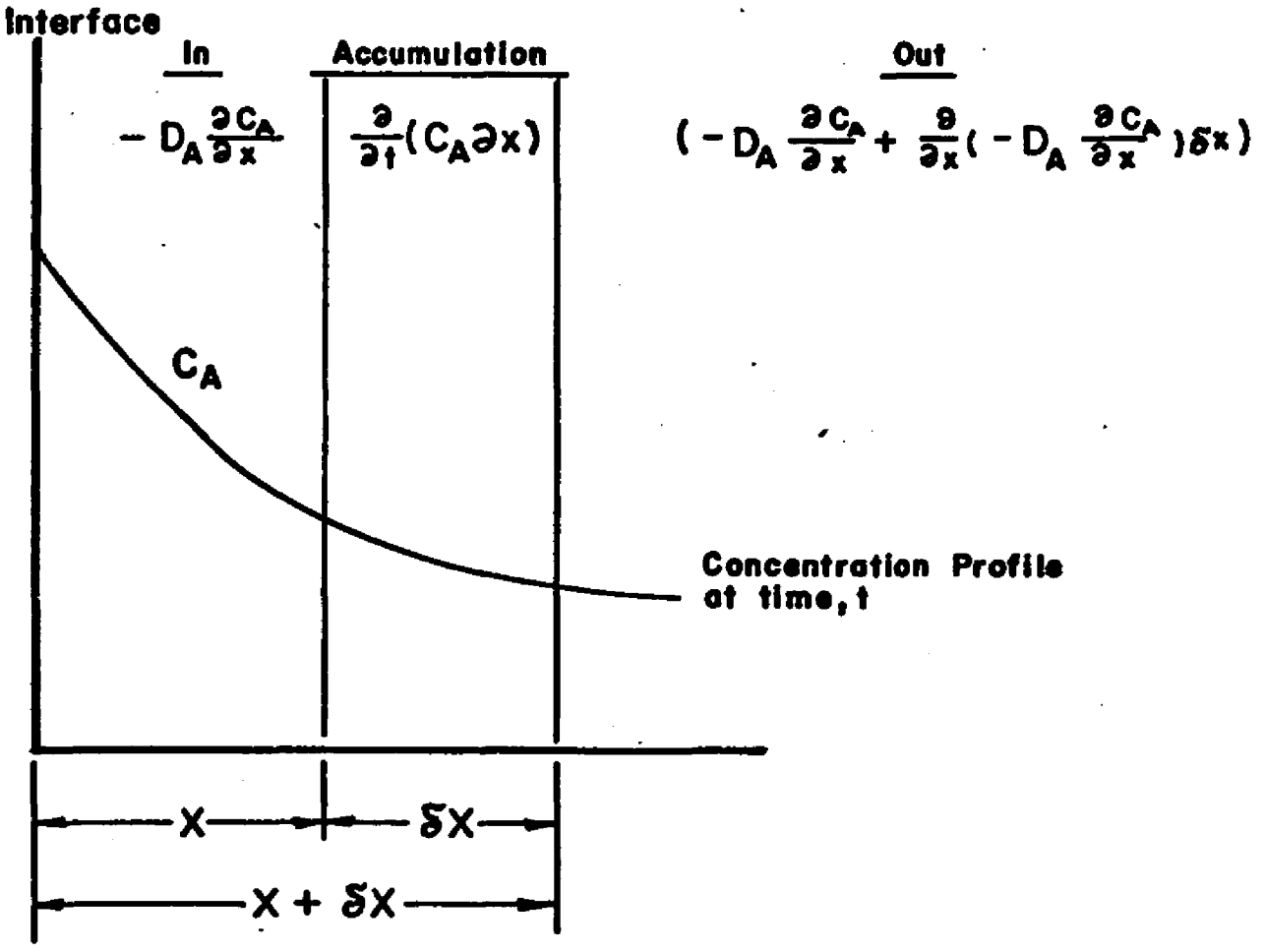

Figure 13, One Dimensional Coordinates for the Derivation Fick's Second Law Leading to the Penetration Theory Solution.

$$D_A \frac{\partial^2 C_A}{\partial x^2} - \frac{\partial C_A}{\partial t} = 0 \qquad (5\text{-}4)$$

The equation can be solved analytically for the particular set of boundary conditions which are maintained with the laminar jet. These boundary conditions are:

1) $t = 0 \qquad C_A = 0$

2) $x = 0 \qquad C_A = C_{A_o}$

3) $x = \infty \qquad C_A = 0$

Using a technique called "the method of combination of variables"[2] the partial differential equation is solved as follows: A solution is anticipated of the form $C_A/C_{A_o} = \chi(\eta)$, in which η is a dimensionless variable $x/\sqrt{4D_A t}$. In terms of the new variables,

$$\frac{\partial (C_A/C_{A_o})}{\partial t} = \frac{\partial \chi}{\partial t} = \frac{\partial \chi}{\partial \eta} \frac{\partial \eta}{\partial t} \qquad (5\text{-}5)$$

$$= -\tfrac{1}{2} \frac{\eta}{t} \frac{\partial \chi}{\partial \eta} = -\tfrac{1}{2} \left(\frac{\eta}{t}\right) \chi' \qquad -$$

and

$$\frac{\partial^2 (C_A/C_{A_o})}{\partial z^2} = \frac{\eta^2}{z^2} \chi''$$

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[2] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena (New York: John Wiley and Sons, Inc., 1960).

where

$$\chi'' = \frac{\partial^2 \chi}{\partial \eta^2}$$

Equation (5-4) becomes:

$$\chi'' + 2\,\eta\,\chi' = 0 \qquad (5\text{-}7)$$

Boundary Condition 1. at $\eta = 0$, $\chi = 1$

Boundary Condition 2. $\eta = \infty$, $\chi = 0$

If χ' is replaced by Ψ, the equation becomes a first order separable differential,

$$\Psi' + 2\,\eta\,\Psi = 0 \qquad (5\text{-}8)$$

and

$$\Psi \equiv \chi' = C_1\, e^{-\eta^2} \qquad (5\text{-}9)$$

$$\chi = C_1 \int_o^{\eta} e^{-\eta^2}\, d\eta + C_2 \qquad (5\text{-}10)$$

Application of the boundary conditions then gives;

$$X = 1 - \frac{\int_o^{\eta} e^{-\eta^2}\, d\eta}{\int_o^{\infty} e^{-\eta^2}\, d\eta} = -\frac{2}{\sqrt{\pi}} \int_o^{\eta} e^{-\eta^2}\, d\eta \qquad (5\text{-}11)$$

The ratio of the integrals is called the error function, abbreviated erf η; evaluated numerically and tabulated in handbooks.[3] The solution of the unsteady state differential equation may be written,

$$C_A/C_{A_o} = 1 - \frac{2}{\sqrt{\pi}} \int_o^{\eta} e^{-\eta^2}\, d\eta \qquad (5\text{-}12)$$

$$= 1 - \frac{2}{\sqrt{\pi}} \text{ erf } \eta \qquad (5\text{-}12a)$$

where C_A = the concentration at any time in the liquid.

C_{A_o} = the concentration of initial conditions.

$\eta = \frac{X}{\sqrt{4D_A t}}$ a dimensionless position variable.

t = the time of contact.

D_A = the diffusion coefficient.

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[3] K. A. Korn and T. M. Korn, Mathematical Handbook for Scientist and Engineers, (New York: McGraw-Hill, Inc., 1961), p. 899.

The local mass flux at a point on the interface x = 0, at a position y down the liquid jet, is;

$$N_A \Big|_{x=0} = - D_{AB} \frac{\partial C_A}{\partial x} \Big|_{x=0} = C_{A_o} \sqrt{\frac{D_{AB}}{\pi t}} \qquad (5\text{-}13)$$

The local flux is integrated over the entire length of the surface to give the working equation:

$$N_A \text{ total} = \int_o^{t'} N_A d\theta = C_{A_o} \sqrt{\frac{D_{AB}}{\pi}} \int_o^{t'} \frac{dt}{t^{\frac{1}{2}}} \qquad (5\text{-}14)$$

$$= C_{A_o} \sqrt{\frac{D_A}{\pi}} \; \frac{t'^{\frac{1}{2}}}{\frac{1}{2}} = 2 \, C_{A_o} \sqrt{\frac{D_A t'}{\pi}} \qquad (5\text{-}14a)$$

The average rate is found by dividing the total quantity by the time of exposure during which this total transfer occurred.

$$N_{A,\ avg.} = 2 \, C_{A_o} \sqrt{\frac{D_A}{\pi t'}} \qquad (5\text{-}15)$$

The equation represents the average mass flux transferred to the liquid jet for a contact time t'. When experimentally measured data of $N_{A,\ avg.}$ is plotted on the basis of, $N_{A,\ avg.}$ versus the reciprocal of the square root of contact time; the result should be a straight line, if the experiment is a good test of the penetration theory. The slope of

the line is equal to $2\sqrt{\frac{D_A}{\pi}}(C_{A_o})$. Knowing the solubility, C_{A_o}, the diffusion coefficient can be computed. As mentioned previously, the laminar jet can be used to measure the diffusion coefficients with very good accuracy.

3. Penetration Theory with Chemical Reaction

The problem of gas absorption accompanied with chemical reaction can be treated by adding an extra "output" term to the unsteady state mass transfer Equation (5-3). Considering the complete system, mass transfer of A occurs across the gas-liquid interface as depicted below:

$$A_{(G)} \rightleftharpoons A_{(L)} \tag{5-16}$$

where it reacts irreversibly with species B as follows,

$$A_{(L)} + \nu B_{(L)} \rightarrow \text{Products} \tag{5-17}$$

The rate of the chemical reaction depicted by Equation (5-17) is assumed to proceed according to the following equation:

$$R = k_F [C_A]^n [C_B]^m \tag{5-18}$$

The parameters k_F, n, and m are assumed constant. For a second order reaction, this rate is represented by Equation (5-18), as,

$$R = k_F C_A C_B \tag{5-19}$$

using this as the other "output" term in the unsteady state mass transfer. The general expression is as follows:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - \frac{\partial C_A}{\partial t} = k_F C_A C_B \tag{5-20}$$

There are two dependent variables C_A, and C_B, and therefore another independent expression for the rate of transfer of B must be derived before any solution is possible.

$$D_B \frac{\partial^2 C_B}{\partial x^2} - \frac{\partial C_B}{\partial t} = k_F C_A C_B \tag{5-21}$$

Both Equations (5-20) and (5-21) can be normalized by letting;

$a = C_A/C_{A_i}$

$b = C_B/C_{B_o}$

$z = (\sqrt{k_F C_{B_o}/D_A})\ x$

$\theta = k_F C_{B_o}\ t$

$r = D_A/D_B$

$q = C_{B_o}/C_{A_i}$

The resulting transformed equations are,

$$\frac{\partial^2 a}{\partial z^2} - \frac{\partial a}{\partial \theta} = ab \tag{5-22}$$

$$rq \frac{\partial^2 b}{\partial z^2} - q \frac{\partial b}{\partial \theta} = ab \tag{5-23}$$

The boundary conditions for the normalized equations are;[4]

At $\theta = 0$, any $z > 0$ $\quad a = 0$

$\quad b = 1$

At $z = 0$, any $\theta > 0$ $\quad a = 1$

$\quad \frac{\partial b}{\partial z} = 0$

At $z \rightarrow \infty$, any θ $\quad a = 0$

$\quad b = 1$

The boundary conditions are satisfied by the laminar jet according to the previous discussion. The condition that a = 0 at the beginning of a contact time requires that the chemical equilibrium is prevailing and $C_A = 0$ throughout the liquid. Peaceman[5] has shown that gas-liquid holdup is sufficient and the assumption is a good one in practical cases.

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[4] P. L. T. Brian, "Gas Absorption Accompanied by an Irreversible Reaction of General Order," A.I.Ch.E. Journal, X (1964), p. 5.

[5] D. W. Peaceman, "Liquid Side Resistance in Gas Absorption With and Without Chemical Reaction," (Sc.D. Thesis, Massachusetts Institute of Technology, 1951).

The desired result from the solution of Equations (5-22) and (5-23) is Φ, the ratio of k_L to k_L^o, (the ratio of the coefficient of absorption with chemical reaction over the coefficient of absorption without chemical reaction). Thus, Φ is a measure of the amount by which simultaneous chemical reaction increases the rate of absorption of species A. Solving the differential equations for a and b as functions of z and θ, Φ can be obtained as follows using dimensional notation in the derivation. At any time the total amount of species A in the liquid per unit cross sectional area is:

$$\int_o^\infty C_A \, dx \tag{5-24}$$

and of B,

$$\int_o^\infty C_B \, dx \tag{5-25}$$

The amount of A consumed by the reaction of A and B is;

$$\int_o^\infty (C_{B_o} - C_B) \, dx \tag{5-26}$$

The total amount of A, which has transferred into the liquid, is obtained by summing the amount present at any time, Equation (5-24), with the amount consumed by reaction with B, Equation (5-26). The average rate of absorption for a contact time t', is obtained by dividing the sum described above by the contact time, t'.

$$\bar{N}_A = \frac{\int_o^\infty C_A dx + \int_o^\infty (C_{B_o} - C_B)\, dx}{t'} \qquad (5\text{-}27)$$

for physical absorption the average rate shown in Equation (5-15), is;

$$\bar{N}_A = 2\, C_{A_i} \sqrt{\frac{D_A}{\pi t'}} \qquad (5\text{-}15)$$

and the coefficient of absorption is

$$k_L^o = \frac{\bar{N}_A}{C_{A_i}} = 2\sqrt{\frac{D_A}{\pi t'}} \qquad (5\text{-}15a)$$

The variable Φ is equal to;

$$\Phi = k_L / k_L^o \qquad (5\text{-}28)$$

Substituting in Equation (5-28) for the coefficients the result is:

$$\Phi = \frac{\int_o^\infty C_A dx + \int_o^\infty (C_{B_o} - C_B)\, dx}{(t')(2)\sqrt{\frac{D_A}{\pi t'}}} \qquad (5\text{-}29)$$

The equation is normalized by letting,

$$a = C_A/C_{A_i}$$

$$b = C_B/C_{B_o}$$

$$z = \left(\sqrt{\frac{D_A}{k_F C_{B_o}}} \right) x$$

$$\theta = k_F C_{B_o} t$$

$$q = C_{B_o}/C_{A_i}$$

and the result is;

$$\Phi = \sqrt{\frac{\pi}{4\theta}} \int_o^\infty [a + q (1 - b)] \, dz \qquad (5\text{-}30)$$

This equation is used to get Φ when values of a and b are obtained as a function of z and θ. The solution of Equations (5-22) and (5-23) is numerical unless two limiting cases are considered: 1) very fast reactions, where Φ is an asymptotic value of very large θ, and, 2) pseudo first order reactions, which removes the non-linearity of Equation (5-22), and allows an analytical solution.

The numerical solution by Brian,[6] et al. was based on the equation of Crank and Nicholson, for time centered, implicit finite differences. The method of solution and the FORTRAN computer program for an I.B.M. 704 computer appears in reference[7]. This program was adapted for this

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[6] Brian, Hurley, and Hasseltine, op. cit.

[7] E. H. Hasseltine and J. F. Hurley, "Solutions of the Penetration Theory for Simultaneous Gas Absorption and Liquid-Phase Chemical Reaction," (S.B. Thesis, Massachusetts Institute of Technology, 1951).

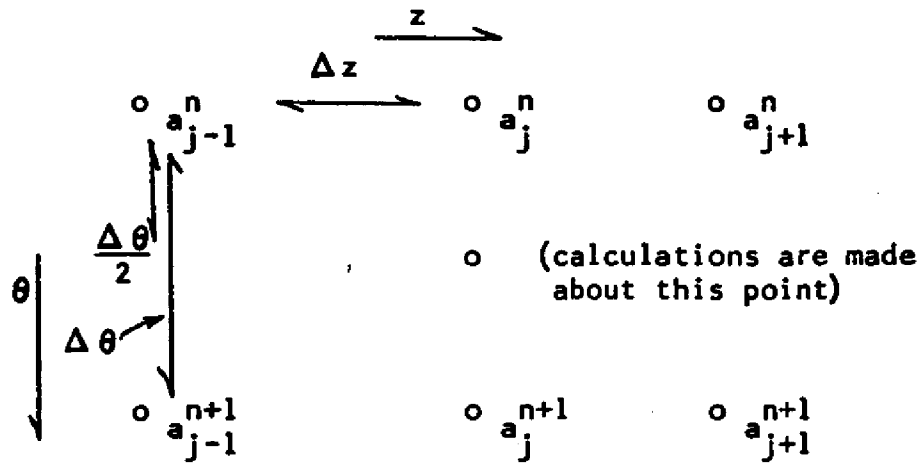
study to extend the range of the published solutions in order to match conditions of physical properties (r, and q) used in this study. A general description of the solution technique follows.

A hypothetical net for the calculation of component A, concentration a_j^n, is arranged as a function of two dimensionless coordinates, time (θ) and distance into the fluid (z).

	Δz_1	Δz_2	Δz_3	Δz_4 . . .	Δz_j
$\Delta \theta_1$	a_1^1	a_2^1	a_3^1	a_4^1	a_j^1
$\Delta \theta_2$	a_1^2	a_2^2			.
$\Delta \theta_3$	a_1^3				.
$\Delta \theta_4$					.
.					.
.					.
.					.
.					.
$\Delta \theta_n$	a_1^n	.	.	. . .	a_j^n

In the implicit method, the surrounding points are used to calculate, the point under study. The forward point values are not all known, so this results in a set of equations which have to be solved simultaneously.

From the following general points, a set of finite difference equations are developed.



$$\left.\frac{\partial a}{\partial z}\right|_{\Delta z_2} \equiv \frac{\dfrac{a^n_{j+1} - a^n_j}{\Delta z} + \dfrac{a^{n+1}_{j+1} - a^{n+1}_j}{\Delta z}}{2} \qquad (5\text{-}31)$$

$$\left.\frac{\partial a}{\partial z}\right|_{\Delta z_1} \equiv \frac{\dfrac{a^n_j - a^n_{j-1}}{\Delta a} + \dfrac{a^{n+1}_j - a^{n+1}_{j-1}}{\Delta z}}{2} \qquad (5\text{-}32)$$

The second partial in the finite difference form is obtained as follows:

$$\frac{\partial^2 a}{\partial z^2} = \frac{\partial a/\partial z \mid_{\Delta z_2} - \partial a/\partial z \mid_{\Delta a_1}}{\Delta z} \tag{5-33}$$

Expanding and combining terms,

$$\frac{\partial^2 a}{\partial z^2} = \frac{a_{j-1}^{n-1} - 2a_j^{n+1} + a_{j+1}^{n+1} + a_{j-1}^{n} - 2a_j^{n} + a_{j+1}^{n}}{2(\Delta z)^2} \tag{5-34}$$

and using standard finite difference notation where,

$$\delta^2 (a_j^{n+1}) = a_{j-1}^{n+1} - 2a_j^{n+1} + a_{j+1}^{n+1}$$

the following expression results.

$$\frac{\partial^2 a}{\partial z^2} = \left[\frac{\delta^2 (a_j^{n+1}) + \delta^2 (a_j^{n})}{2 (\Delta z)^2} \right] \tag{5-35}$$

The finite time difference equation is,

$$\frac{\partial a}{\partial \theta} = \frac{a_j^{n+1} - a_j^{n}}{\Delta \theta}$$

By expressing Equation (5-22) and (5-23) in finite difference notation, the result is:

$$\left[\frac{\delta^2 (a_i^{n+1}) + \delta^2 (a_i^n)}{2 (\Delta z)^2} \right] - \left[\frac{a_i^{n+1} - a_i^n}{\Delta \theta} \right] = \left[\frac{a_i^{n+1} + a_i^n}{2} \right] b_j^{n+\frac{1}{2}} \qquad (5\text{-}36)$$

$$rq \left[\frac{\delta^2 (b_i^{n+1}) + \delta^2 (b_i^n)}{2 (\Delta z)^2} \right] - q \left[\frac{b_i^{n+1} - b_i^n}{\Delta \theta} \right] = \left[\frac{b_i^{n+1} + b_i^n}{2} \right] a_j^{n+\frac{1}{2}} \qquad (5\text{-}37)$$

From the boundary conditions the values of a_j^n and b_j^n were known at time step n, for j = 0, 1, 2, ... J. Since the solution is simultaneous, first, values of $b_j^{n+\frac{1}{2}}$ had to be calculated using an explicit finite difference method before the set of a_j^n values could be calculated. The values of a were inserted in Equation (5-37) to get a set of late time values of b_j^{n+1}. The next time step the order in which the equations were used was reversed. The a values were calculated and inserted in Equation (5-36) and the set of tridiagonal equations were solved. This proceeded from one time step to the other up to the time limit desired for the solution.

The initial row and column values of a are known from the boundary conditions a = 0, at $\theta = 0$, any $z > 0$, and a = 1, at z = 0, any $\theta > 0$. Only the first row of b are known (b = 1) and the first column (for B.C. 2, $\partial b/\partial z = 0$) was calculated by assuming that values of b are represented by a polynomial.

$$b = \alpha + \beta z + \gamma z^2 + \delta z^3 \qquad (5\text{-}38)$$

$$b_o^o = \alpha \qquad (5\text{-}38a)$$

$$b_1^o = \alpha + \beta\,(\Delta z) + \gamma\,(\Delta z)^2 + \delta\,(\Delta z)^3 \qquad (5\text{-}38b)$$

$$b_2^o = \alpha + \beta\,(2\Delta z) + \gamma\,(2\Delta z)^2 + \delta\,(2\Delta z)^3 \qquad (5\text{-}38c)$$

$$b_3^o = \alpha + \beta\,(3\Delta z) + \gamma\,(3\Delta z)^2 + \delta\,(3\Delta z)^3 \qquad (5\text{-}38d)$$

Since $\partial b/\partial z = 0$, $\beta = 0$. Solving the system of equations for the coefficients the results are:

$$b_o^n = \frac{18}{11}\,b_1^o - \frac{9}{11}\,b_2^o + \frac{2}{11}\,b_3^o \qquad (5\text{-}39)$$

The boundary conditions used in the finite difference methods were:

$$a_j^o = 0$$

$$b_j^o = 1 \qquad \text{for } j = 0,\ 1,\ 2,\ \ldots\ J$$

and from Equation (5-39) the other boundary conditions were

$$a_o^n = 1$$

$$b_o^n = \frac{18b_1^n - 9b_2^n + 2b_3^n}{11} \qquad \Big\} \; n = 1,\ 2,\ 3$$

The result desired from the solution of these concentration nets of A and B is the ratio Φ as defined above, by Equation (5-30).

$$\Phi = \frac{\pi}{4\theta}\int_o^\infty [a + q\,(1 - b)\,]\,dz \qquad (5\text{-}40)$$

For the values of a and b calculated as described above, the integration was performed numerically using Simpson's Rule. The upper limit of the integration over z is out to ∞, but in reality this was carried out only to large values of z, and the boundary conditions (a = 0, b = 1) were approached.

With this model, Φ can be calculated for any system which follows the penetration theory, and compared with the experimental results obtained for the particular system. Computing a single curve, which is the numerical solution at a specific r and q for Φ versus θ (or $\sqrt{m}$) out to its asymptotic value requires as long as 4 hours on the I.B.M. 7040 electronic computer. Figure 14 shows such a curve computed for q = 10.37, and q = 4.33 at r = 2.91. The values of r and q's are at the conditions used in series of runs at the higher sodium hydroxide concentrations. This curve was used to get an estimate of the reaction rate constant, k_F, which was the only parameter not measured, except by this estimation procedure.

4. Infinitely Rapid Chemical Reaction

For given values of r and q the variable Φ, in the solution described above, approaches an asymptotic value at large values of θ. This asymptote Φ_a, r, and q has been obtained analytically by Danckwerts[8] and by Sherwood and Pigford[9] and presented by Brian[10]

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[8] P. V. Danckwerts, "Absorption by Simultaneous Diffusion and Chemical Reaction," Transactions of the Faraday Society, XLVI (1950), p. 300

[9] T. K. Sherwood and R. L. Pigford, Absorption and Extraction, (2nd Edition; New York: McGraw-Hill, Inc., 1952), pp. 317-339.

[10] Brian, op. cit.

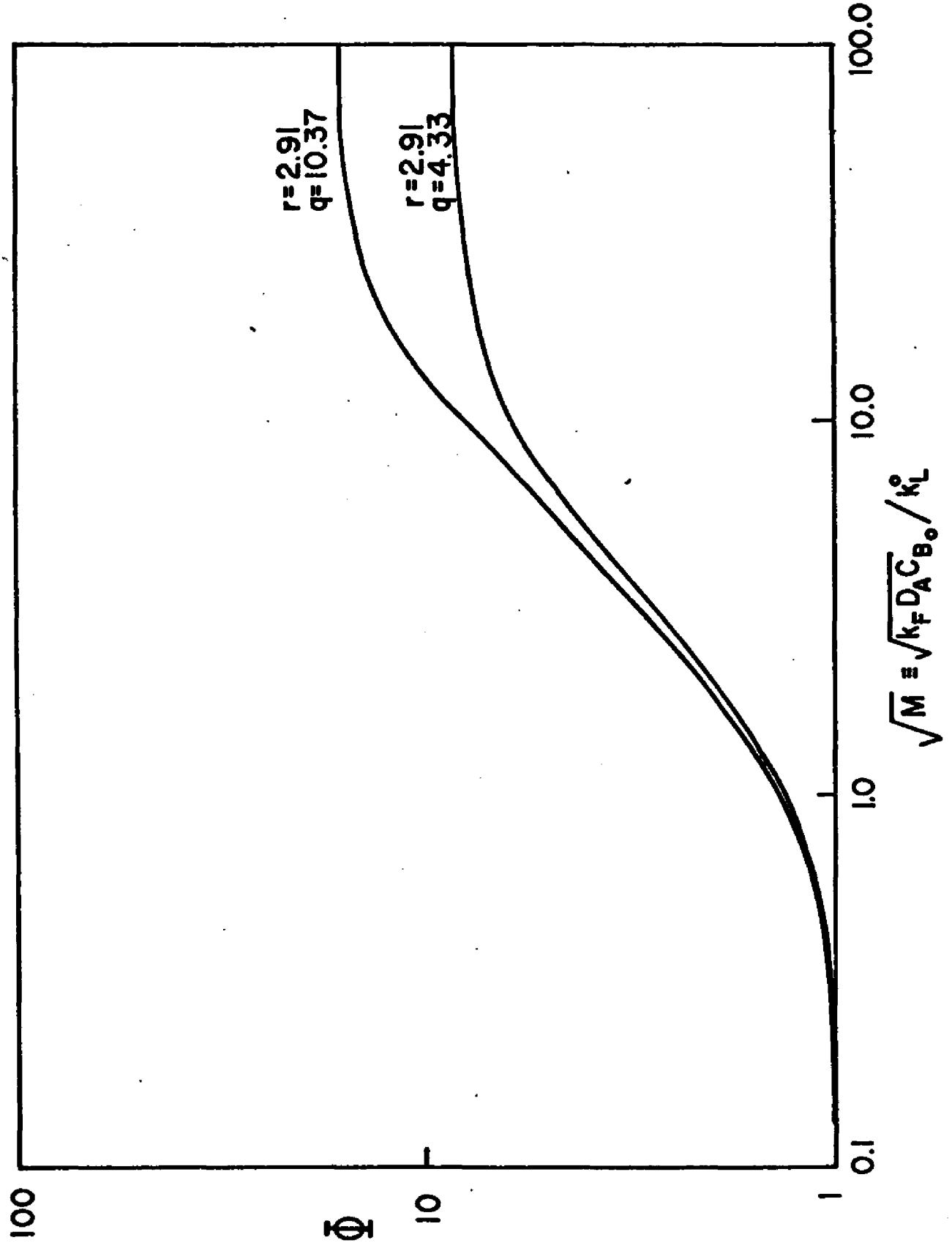

Figure 14, Theoretical Solution for Penetration Theory Absorption with Second Order Irreversible Chemical Reaction.

in the following form,

$$\Phi_a = 1/\text{erf}\ (\sigma)$$

$$q\sqrt{r} = \frac{1 - \text{erf}\ (\sigma/\sqrt{r})}{\text{erf}\ (\sigma)\ \exp\ [\sigma^2\ (1-1/r)]} \qquad (5\text{-}41)$$

These are parametric equations, with σ as a dummy parameter used to generate values of Φ_a versus $q\sqrt{r}$ as shown in Figure 15. From this plot it can been seen that the penetration theory solution for infinitely fast chemical reaction can be expressed by the following simplified relationships:

$$\Phi_a = 1 + q \qquad \text{when } r = 1 \qquad (5\text{-}42)$$

$$\Phi_a \cong 1 + q\sqrt{r} \qquad \text{when } r \neq 1 \qquad (5\text{-}43)$$

This simplification is particularly useful in packed tower design calculations for absorption with fast reactions. The concept is used in a later section on absorber design, and also used to compare the data from the laminar jet with the predicted solutions.

5. Empirical Correlation of the Numerical Solutions

An empirical correlation of the general numerical solutions facilitates the use of the penetration theory by greatly reducing computation time, eliminating duplication of effort, and making the

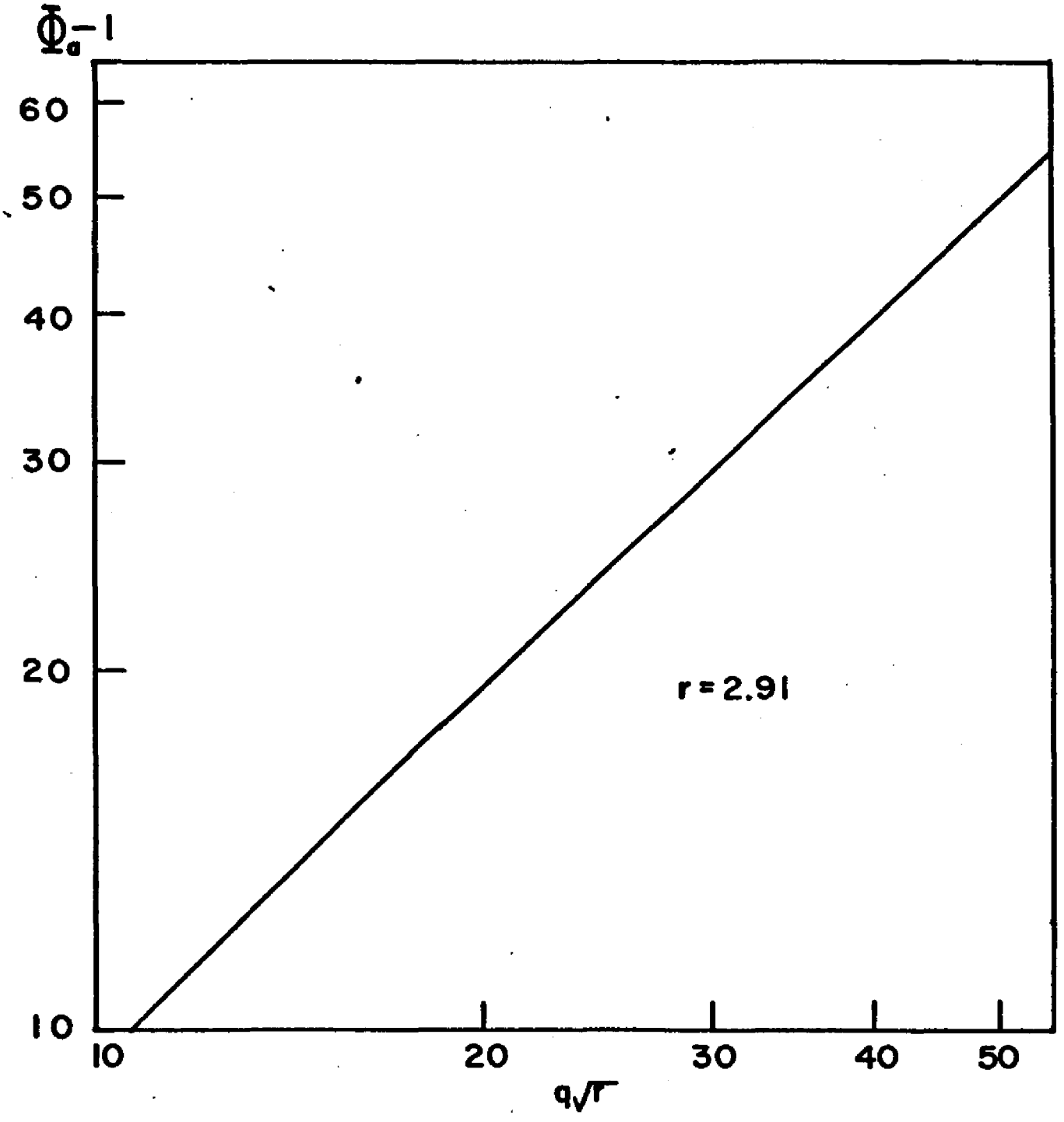

Figure 15, Theoretical Solution for an Infinitely Fast Second Order Chemical Reaction

use of these solutions practical in absorption tower design programs. Brian[11] developed a correlation based on the assumption of equal diffusivities; i.e. the solute and the liquid phase reactant have equal diffusivities in liquid phase. The correlation was developed mainly for interpolations, but in this work it was found suitable for extrapolations which turned out to be much more accurate than reading directly off of the small published plots.

The correlation equation for a second order reaction is:

$$\left[\frac{(\sqrt{M})_q}{(\sqrt{M})_{\text{pseudo, 2nd order}}}\right]_{\text{same } \Phi} = \left(\frac{\Phi_a - 1}{\Phi_a - \Phi}\right)^{.4} \qquad (5\text{-}44)$$

where

$(\sqrt{M})_q$ = is the relative rate parameter described previously, a function of contact time

$(\sqrt{M})_{\text{pseudo, 2nd order}}$ = the relative rate parameter for a pseudo 2nd order reaction

In the evaluation of Φ for pseudo order reactions, it was found that the maximum deviation between the solution of zero order reaction and a third order reaction was a maximum of 3%. The deviation between second order and first order was a maximum of 1%, with this error

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[11] Brian, op. cit.

decreasing as the contact times ($\sqrt{M}$) increases. This small deviation allowed the use of the analytical solution (Equation (5-45)) for pseudo first order as a good approximation for the pseudo second order solutions, which requires a numerical analysis solution. The analytical solution for the absorption with a pseudo first order chemical reaction is;[12,13]

$$\Phi_a = \sqrt{M}\left[1 + \frac{\pi}{8M}\right] \operatorname{erf} \sqrt{\frac{4M}{\pi}} + \tfrac{1}{2} \exp\left(-\frac{4M}{\pi}\right) \qquad (5\text{-}45)$$

The use of this expression makes the correlation expression even more versatile, because now values of Φ versus $\sqrt{M}$ can be obtained in a very short time by a computer as part of a design program. The solution of these values require a successive approximations, since Φ cannot be solved for explicitly from Equation (5-44) and (5-45). The details of this iterative technique is given in Appendix E.

6. Extension of Theory to Packed Absorber Design

The design of packed absorbers for gas absorption with simultaneous chemical reaction can be readily accomplished if the mass transfer process over the entire tower is gas phase limiting. Usually the liquid phase reactant will drop below a certain level, the reaction effect will decrease, and the liquid phase resistance will become significant. This shift could make the tower operation unsatisfactory if the design was based on strictly gas phase limiting assumption. If the reaction

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[12] Sherwood and Pigford, op. cit.

[13] Brian, op. cit.

rate is slow, or moderate, the liquid phase resistance may be significant throughout the column.

When the reaction is very fast the tower design can be accomplished by a simple technique presented by Secor and Southworth.[14] The method will be called the integral method, to distinguish it from the differential technique developed in this work.

a. Integral Method

The integral method considers the absorption process occurring in three zones: (1) the surface reaction zone with no liquid phase resistance, (2) the interior reaction zone, where the mass transfer is influenced by diffusion of liquid reactant and gaseous solute, and (3) physical absorption after the liquid reactant is exhausted. The shift from surface reaction zone to interior reaction occurs at a critical concentration which can be evaluated readily. Actually the change is continuous and can be handled another way. The derivation of the equations are straightforward and is described in Appendix F. The resulting integrated equations for the solution of packed height are given here as an introduction to the next method. The height of the surface reaction zone, which is at the top of the column as shown in Figure 16, can be obtained by integration of the following equations. A material balance for a differential length of tower is given by

$$N_A a = G_M \frac{dy}{dh} \qquad (5\text{-}46)$$

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[14] R. M. Secor and R. W. Southworth, "Absorption With an Infinitely Rapid Chemical Reaction in Packed Towers," A. I Ch. E. Journal, VII (1961), p. 705.

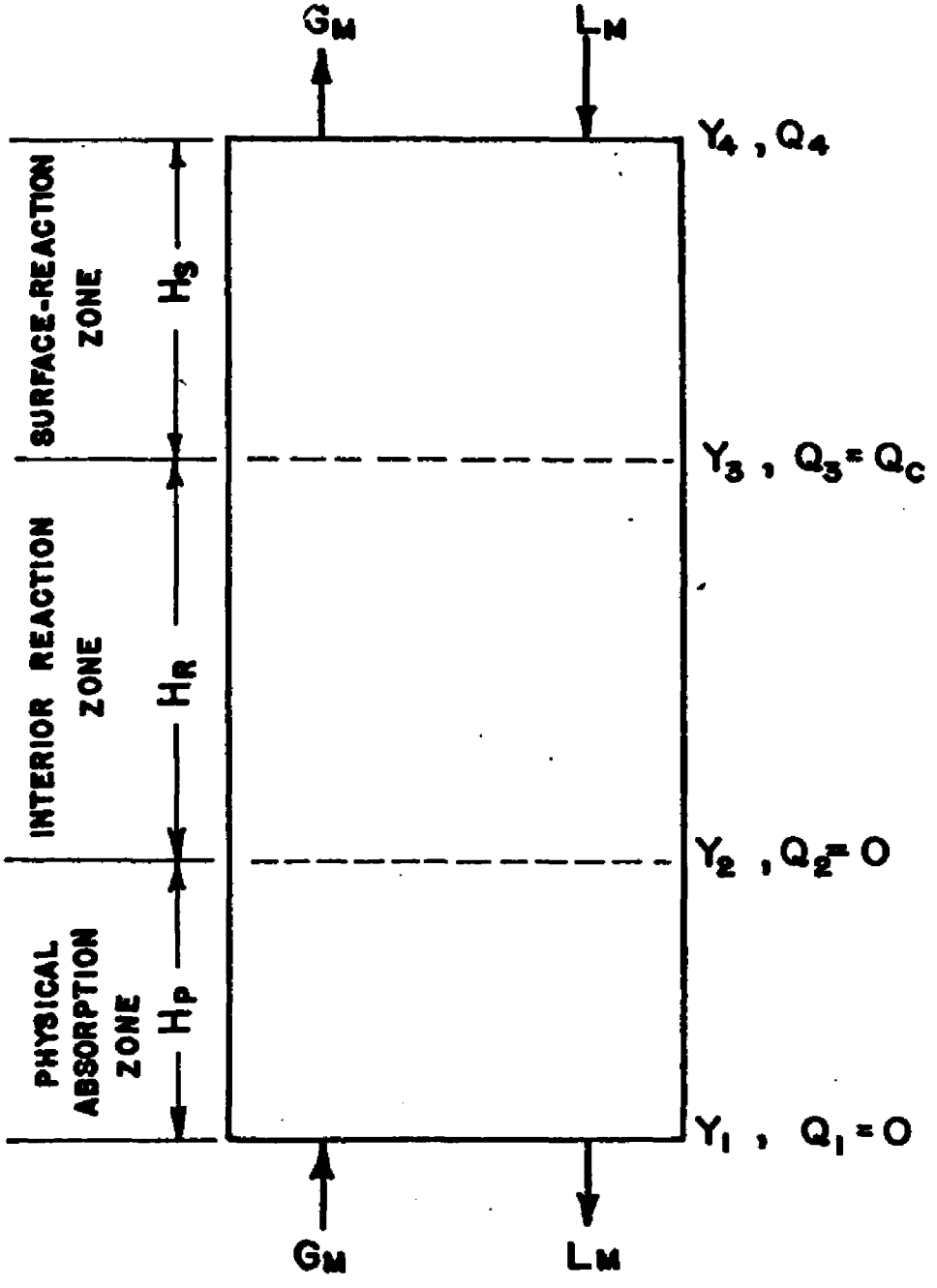

FIGURE 16, REPRESENTATION OF THE THREE ABSORPTION ZONES IN A PACKED TOWER IN WHICH THE REACTION A+B → AB TAKES PLACE AT AN INFINITELY RAPID RATE.

and the rate equation is

$$N_A a = k_G a\ P\ (y - 0) \tag{5-47}$$

because there is no liquid phase resistance, and the bulk liquid phase concentration of the gaseous solute is zero since the reaction is immediate. Assuming $(G_M/k_G a\ P)$ is constant one gets,

$$h_s = \frac{G_M}{k_G a\ P} \ln y_3/y_4 \tag{5-48}$$

The height of the interior reaction zone is obtained by applying the same material balance represented by Equation (5-46). The rate expression for the interior reaction zone which is obtained by manipulation the Hatta film theory equation and applying initial conditions to an overall material balance over the interior reaction zone section can be simplified to,

$$N_A a = k_G a\ P\ (\alpha y + \beta) \tag{5-49}$$

The constants α and β contain physical parameters such as diffusion coefficients of A and B. The simple expression can be integrated to obtain the height of the interior reaction zone. Starting with the following differential equation,

$$G_M \frac{dy}{dh} = K_G a\ P\ (\alpha y + \beta) \tag{5-50}$$

and integrating over the concentration limits, the following expression for height results.

$$h_1 = \frac{G_M}{K_G a P} \frac{1}{\alpha} \ln \left(\frac{\alpha y_2 + \beta}{\alpha y_3 + \beta}\right) \qquad (5\text{-}51)$$

The height of the physical absorption zone is the same given by Colburn,[15] namely,

$$h_p = \frac{\frac{G_M}{K_G a P} \ln \left[\left(1 - \frac{mG_M}{L_M}\right) \frac{y_1}{y_2} + \frac{mG_M}{L_M}\right]}{1 - \frac{mG_M}{L_M}} \qquad (5\text{-}52)$$

The total height of an absorption tower is the sum of the individual heights. Knowing the physical parameters, gas and liquid absorption coefficients, the concentration of the inlet liquid reactant, and the inlet and outlet gas concentrations, the height of the tower can be solved for directly.

b. Differential Method

A method for the solution of packed tower height and prediction of outlet concentrations was developed in the course of this study for the extension of laboratory model. The differential technique was

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[15] A. P. Colburn, "The Simplified Calculation of Diffusional Processes," Transactions of the American Institute of Chemical Engineers, XXXV (1939), p. 211.

patterned on the surface renewal penetration theory. In the solution a differential element of the tower roughly equal to the height of a piece of packing was chosen. This concept is used to get a value of Φ for a certain contact time, and to obtain a measure of the effect of reaction on the gas absorption rate.

A column of unknown height was incremented in differential elements representing changes in the bulk gas phase concentration. Figure 17 shows the packed absorber schematically. With terminal conditions known, and starting at the top of the column, the first initial increment was considered. A material balance around the element was used to get the liquid phase concentration leaving the element. The next step was to consider the interfacial concentration of the gaseous species. For the limiting case, with very concentrated liquid solutions of reactants the interfacial concentration was essentially zero, and the computer method considered the solution as a very small but finite number. The calculation of the interfacial concentration was a trial and error procedure since it is a function of mass transfer rate; and, the liquid phase mass transfer rate is a function of the interfacial concentration as indicated by the parameter used in the numerical penetration theory solution, $q = C_{B_o}/C_{A_i}$. As shown in Equation (5-43), q is also used to evaluate Φ when the reaction rate is infinitely fast.

$$\Phi_a \cong 1 + \sqrt{rq} \qquad \text{where } q = C_{B_o}/C_{A_i} \tag{5-53}$$

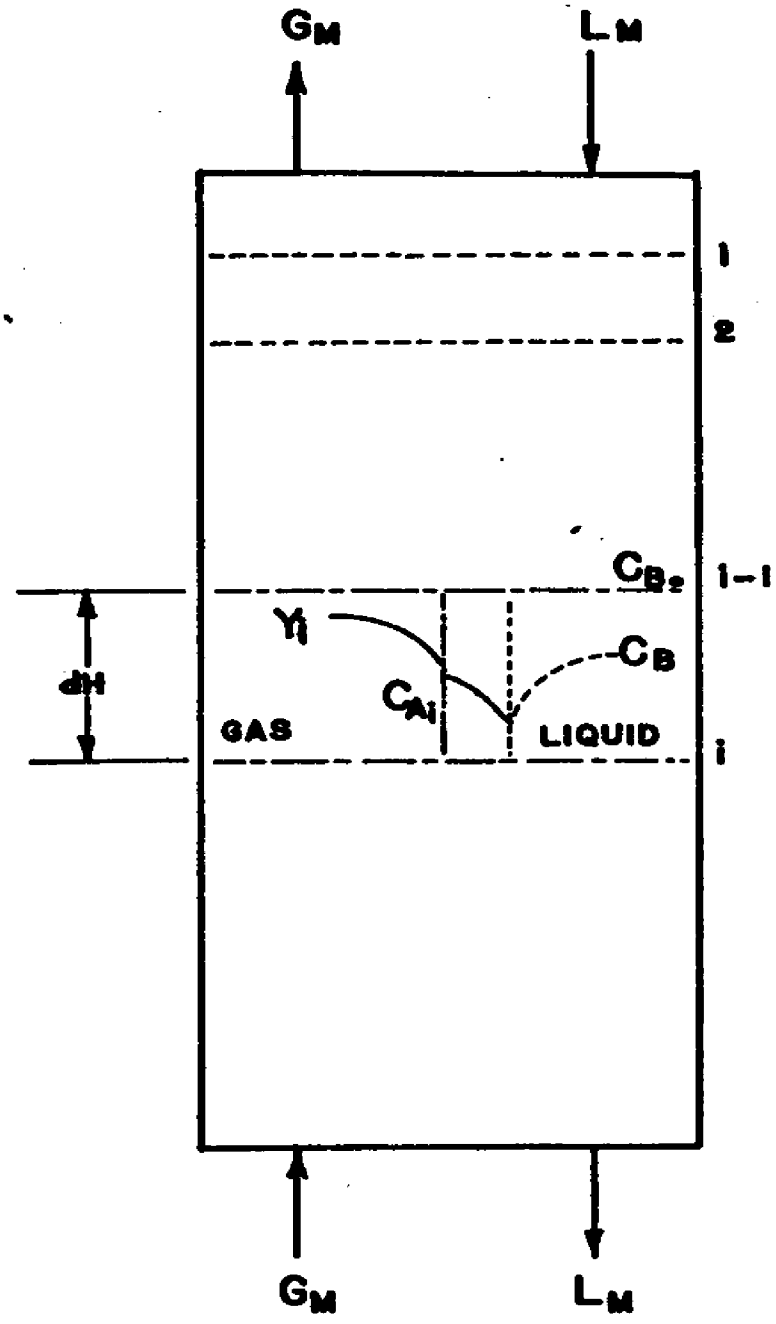

FIGURE 17 , REPRESENTATION OF REACTION ZONE IN PACKED ABSORBER

The procedure to evaluate, C_{A_i}, the interfacial concentration, is as follows:

(a) estimate C_{A_i} assuming no gas phase resistance using Henry's Law constant.

$$C_{A_i} = H/y_{bulk}$$

(b) evaluate Φ from the empirical correlation by estimating q from the initial calculation of C_{A_i}, $q = C_{B_o}/C_{A_i}$.

(c) Calculate a new estimate of C_{A_i}, using the Φ value in the mass transfer expression.

$$N_A = k_L a\ (C_{A_i} - 0) = k_G a\ (y - y_i) \qquad (5\text{-}54)$$

$$= \Phi\, k_L^o a\ C_{A_i} = k_G a\ (y - HC_{A_i}) \qquad (5\text{-}55)$$

Solving for C_{A_i}, one gets

$$C_{A_i} = \frac{k_G a\ y}{\Phi\, k_L^o a + H\ k_G a} \qquad (5\text{-}56)$$

(d) The late value of C_{A_i} is used again in (b) to calculate a new C_{A_i}; and the process repeated until the value of $K_G a$ converges to a test limit.

(e) In (b) the evaluation of Φ requires a trial and error procedure described in Appendix E.

The solution proceeds in this manner from one increment to the next storing the late values of $K_G a$ and y.

The solution for the height of the column is based on the following derivation.

$$N_A = G_M \frac{dy}{dn} = K_G a \ (y - 0) \qquad (5\text{-}57)$$

Solving the equation for the height,

$$h = \int_{y_2}^{y_1} \frac{G}{K_G a} \frac{dy}{y} \qquad (5\text{-}58)$$

Since $K_G a$ is a variable and not an explicit function of y, the equation must be integrated numerically. Using Simpson's rule the stored values of $K_G a$ and y for each element are summed to give the height of the tower. A computer program was written in FORTRAN IV language for an I.B.M. 7040 digital computer based on the above method.

The computer program in Appendix G was used in predictive design and compared with absorption data obtained for the National Council for Stream Improvement by Jensen.[16] The absorption of the dilute methyl mercaptan-air mixture was obtained in a 2 in. diameter tower

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[16] G. A. Jensen, Final Report on Absorption of Odor Producing Sulfur Compounds, to National Council for Stream Improvement, December 31, 1964.

packed with 1.7 feet of 1/4 inch Intalox saddles. The tower with usual auxillary equipment was operated at twelve levels of sodium hydroxide concentrations. Multiple chromatographic analyses were made to determine inlet and outlet concentrations. Initial evaluation of the data was limited to the calculation of the $K_G a$, which wasn't constant and could not be scaled up, since it was based on the following integral

$$\int_o^h dh = \int_{y_2}^{y_1} \frac{G_M}{K_G a\ P} \frac{dy}{y} \qquad (5\text{-}59)$$

which defines $K_G a$ only if the ratio $G_N/K_G a\ P$ is constant. This is true only for the limiting cases where gas phase resistance controls and when reaction effects are negligible. The data could not be scaled up unless a more realistic model was developed. Using the data obtained in laboratory study: second order mechanism, D_{CH_3SH}, D_{OH^-}, k_F and solubility, a successful model was developed. Figure 18 shows the original data.

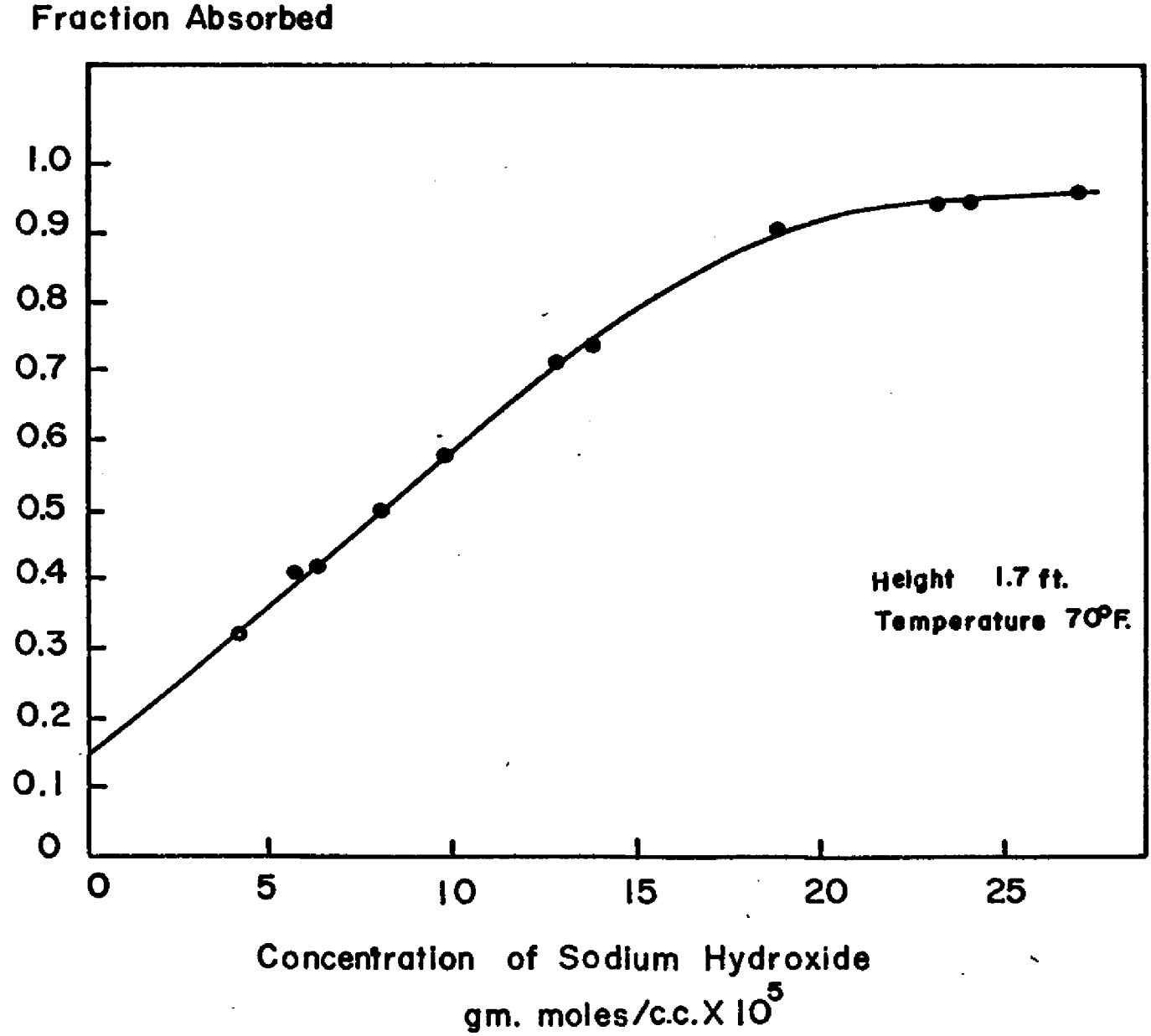

Figure 18, Packed Pilot Absorber Results – Fraction Absorbed Under Changing Liquid Feed Concentration of Sodium Hydroxide.

CHAPTER VI

DISCUSSION OF RESULTS

1. Carbon Dioxide and Water

The laminar liquid jet was designed to contact the absorbing liquid with a gas for a short period of time under conditions in which the jet mass transfer area, contact time, and absorption rate could be determined. The equipment was designed according to the best engineering technology available, particularly orifice design and precision machining. The mass transfer area was determined by calibration with a travelling microscope as described in the experimental section in Chapter IV. The contact area was determined to be free of ripples by visual examination under a microscope. The gas absorption rate was determined accurately with a bubble film flow meter also described previously. The contact time was calculated by using a measured diameter and the assumption of plug flow. This assumption had to be justified before equipment reliability and calibration of the technique was ascertained. Using a system which had previously been well investigated, regarding the determination of the diffusion coefficient and solubility, the instrument was evaluated. Any discrepancies in the results was attributable to the errors in the flow regime assumption and the method of calculation of contact time. Carbon dioxide and water suited these criteria.

The use of a square edged diaphragm orifice produces laminar liquid jets with only a slight initial boundary layer retardation. This effect is insignificant except under the shortest contact times. Bell mouthed orifices produce considerable boundary layer retardation and this shows up in the plot of the data. Figure 19 shows the effect as determined by Raimondi and Toor[1] for a bell mouthed orifice on the carbon dioxide-water system. Knowing the velocity profile for the bell orifice, a correction can be added, which is based on approximate boundary layer theory solutions. The use of thin-square edged orifices eliminates the need for the correction and a test of the data usually shows that the plug flow assumption is adequate.

In order to test the penetration theory solution, the best value for the diffusivity of CO_2 in water at 25°C was used. The most recent values for D are: 1.97×10^{-5}[2] and 1.95×10^{-5}[3] $cm.^2/sec.$ The mean value of 1.96×10^{-5}[4] $cm.^2/sec.$ was taken and used for comparison in this work. The solubility of CO_2 in water was taken to be .759 cc. (NTP) per cc.[5] With these two physical constants, Equation (3-20)

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[1] P. Raimondi and H. L. Toor, "Interfacial Resistance in Gas Absorption," A.I.Ch.E. Journal, V (1959), p. 86.

[2] J. F. Davidson and E. J. Cullen, "The Determination of Diffusion Coefficients for Sparingly Soluble Gases in Liquids," Transactions of the Institution of Chemical Engineers (London), XXXV (1957), p. 51.

[3] T. R. Rehm, (M.S. Thesis, University of Washington, 1960).

[4] J. K. A. Clarke, "Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times," Industrial and Engineering Chemistry - Fundamentals, III (1964), p. 211.

[5] International Critical Tables, Vol. 3., (New York: McGraw-Hill, Inc., 1928), p. 259.

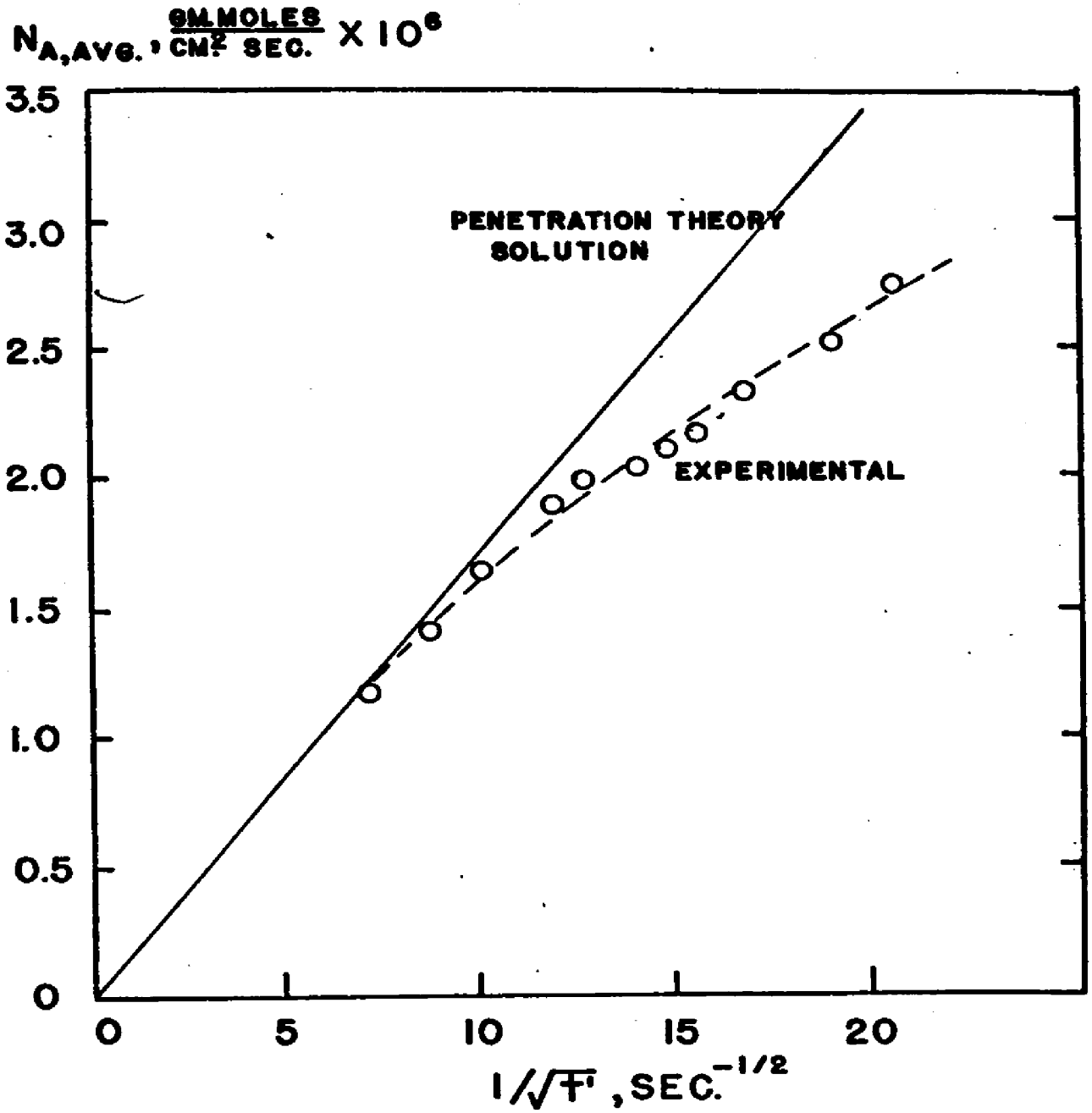

FIGURE 19, RATE OF ABSORPTION OF CARBON DIOXIDE IN WATER. JET WITH PARABOLIC VELOCITY PROFILE.

was used to predict the penetration theory results.

$$\bar{N}_A = 2\,(C^*)\sqrt{\frac{D_A}{\pi t'}} \qquad (3\text{-}20)$$

The equation for the theoretical line, after insertion of the constants, is;

$$\bar{N}_A = (2)(3.39 \times 10^{-5}\ \frac{\text{gm. mole}}{\text{cc.}}\sqrt{\frac{1.96 \times 10^{-5}}{(3.14)(t')}} \qquad (6\text{-}1)$$

$$\bar{N}_A = 1.70 \times 10^{-7}\ \frac{1}{\sqrt{t'}} \qquad (6\text{-}1a)$$

The system CO_2 and water was studied at 25°C. A total of 66 observations over 14 runs were made at various contact times. The contact times were controlled by varying the jet length and liquid flow rate. Varying the jet length also varies the mass transfer area so that system errors and interdependence between the variables can be checked out. The tabulated data is given in Appendix B, and the results are plotted in Figure 20.

The results obtained with the laminar jet follow very closely the theoretical line of the penetration theory result. The maximum deviation is at the high values of $1/\sqrt{t'}$ which was short contact times in the order of 3 milliseconds. At these short contact times and jet lengths, the boundary layer retardation and the end effects were the jet meets the receiver, is obviously significant. The other points are linear and distributed about the theoretical line.

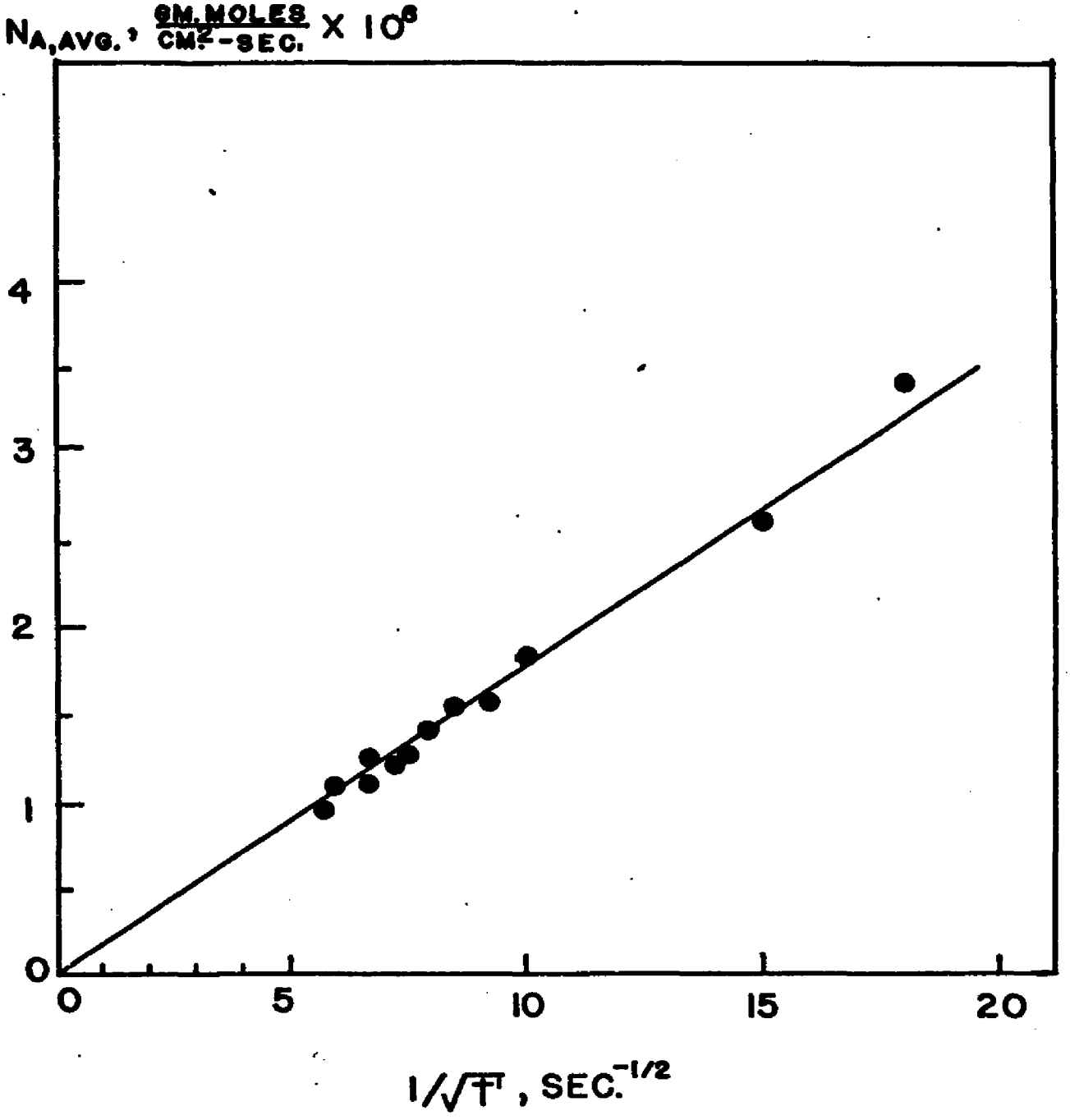

FIGURE 20, ABSORPTION OF CARBON DIOXIDE IN WATER AT 25° C.

At this point the results from the CO_2-Water system was taken as sufficient proof of the accuracy of the apparatus, and the laminar jet was used with confidence on unknown systems. The method of calculation of contact times was also accurate.

2. Sulfur Dioxide and Water

In order to test the laboratory facilities and the experimental technique for the operation with toxic gases, the system sulfur dioxide and water was tested. Using sulfur dioxide, brought in another magnitude of difficulty in the experimental technique, since all purging and excess gas vents had to be controlled. The liquid effluent from the laminar jet was collected and transported to an external waste disposal point. The use of the sulfur dioxide also provided the means for a check on the bubble film flowmeter because of the availability of an accurate titrimetric method for sulfurous acid.

The rate of absorption of SO_2 into the liquid jet was measured by the bubble film flowmeter. The liquid effluent with the absorbed SO_2 was piped through a closed system to an automatic pipette. Three aliquots of the liquid effluent was drawn into solutions with a known equivalent weight of iodine. The excess iodine was titrated with thiosulfate and the SO_2 determined by difference. Knowing the liquid rate, the amount absorbed was calculated and compared with the quantity measured by the bubble film gas burette. Agreement was satisfactory as shown in Table II, with the discrepancy caused by some loss of SO_2 in the titration step.

The data obtained in the study on sulfur dioxide is plotted in Figure 21. As predicted by the penetration theory (Equation (3-20))

TABLE 11

TEST OF BUBBLE FILM FLOWMETER

Millequivalents* in Aliquot	Flow Factor	Rate of SO_2 Titrated cc./min.	Rate of SO_2** Volumetric cc./min.	% Diff.
.125	28.3	87	90.0	- 3%
.135	15.1	50	52.5	- 5%
.512	6.	75.5	78.0	- 3%

* 3 samples from 10 ml. automatic pipette

** mean observation on bubble film flowmeter 3 - 5 observations

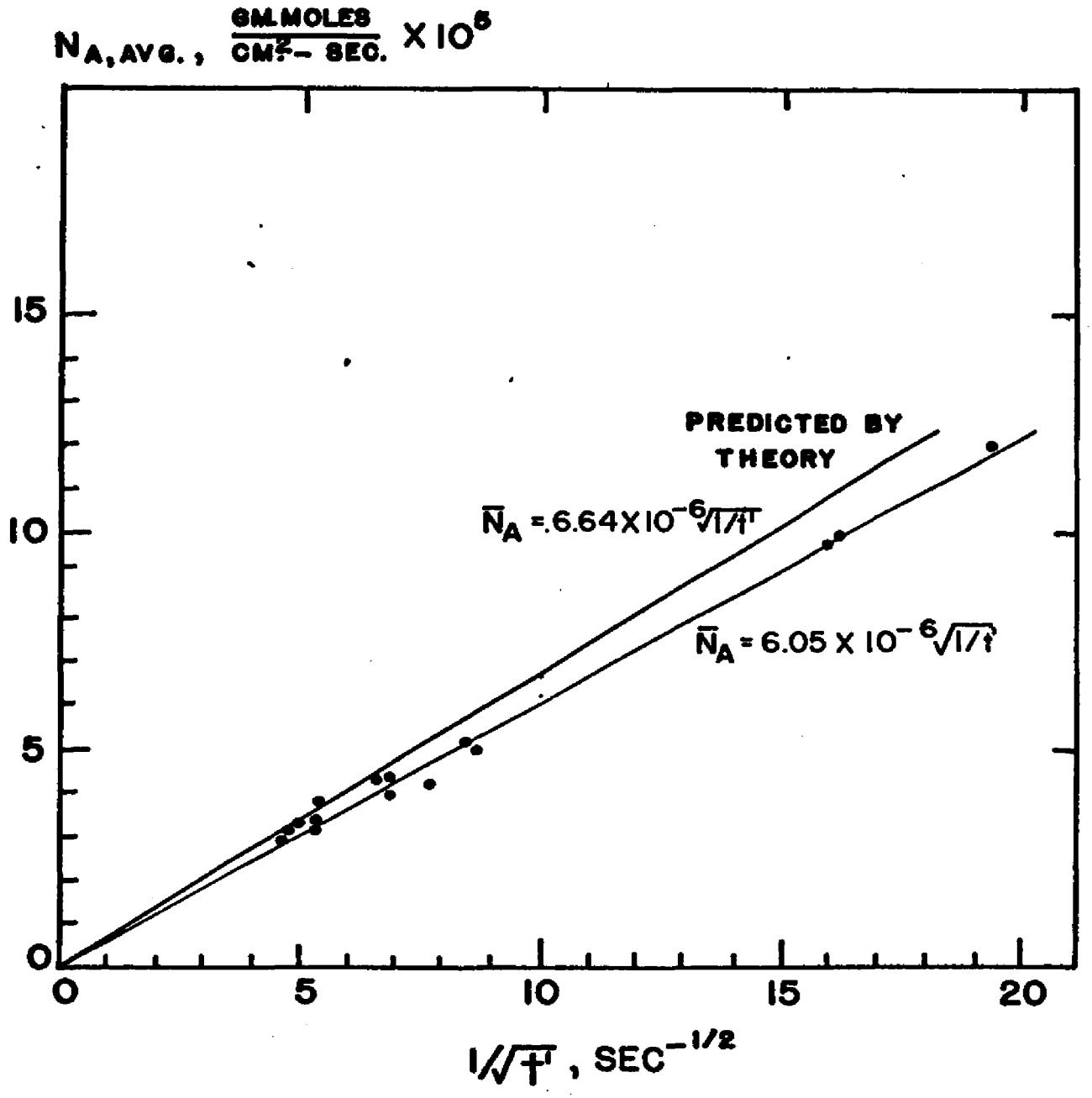

FIGURE 21, ABSORPTION OF SULFUR DIOXIDE IN WATER AT 25°C.

the plot of N_A versus $1/\sqrt{t'}$ gives a linear relationship. Literature values for the diffusion coefficient vary widely probably due to the reaction effects of the SO_2 with water and also the very high solubility which would give rise to concentration effects on the diffusion coefficient. Cited values of D_L range from 2.05×10^{-5} to 1.7×10^{-5} cm.^{2}/sec. As a result both values were used to calculate the theoretical lines. The solubility was taken from some recent work by Rabe and Harris[6] which should be accurate. A plot of the isotherms are presented in Figure 22. At 25°C and 754 mm. of Hg the solubility of SO_2 1.30×10^{-3} gm.-moles/cc. (8.3 gms./100 gms. H_2O). This differs considerably from some old data[7] which lists the solubility as 1.43×10^{-3} gm.-moles/cc.; the value which is usually found in the handbooks. Using these two physical parameters, the diffusion coefficient and the solubility, a theoretical line giving the lower estimate of flux (using D_{SO_2} = 1.7×10^{-5} cm.^{2}/sec.) was calculated from the following expression

$$\bar{N}_A = 6.05 \times 10^{-6} \sqrt{\frac{1}{t'}} \qquad (6\text{-}2)$$

The theoretical line giving the higher estimate was calculated from Equation (6-3) where the $D_{SO_2} = 2.05 \times 10^{-5}$ cm.^{2}/sec. was used.

$$\bar{N}_A = 6.64 \times 10^{-6} \sqrt{\frac{1}{t'}} \qquad (6\text{-}3)$$

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[6] A. E. Rabe and J. F. Harris, "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water," Journal of Chemical and Engineering Data, VIII (1963), p. 3.

[7] F. Schoenfeld, "Ueber den Absorptions Coëfficient en den Schwefligen Säure, des Chlorsund Schwefelwasserstoffs," Annalen der Chemie und Pharmacie, Justus Liebigs, XCV (1855), pp. 1-23.

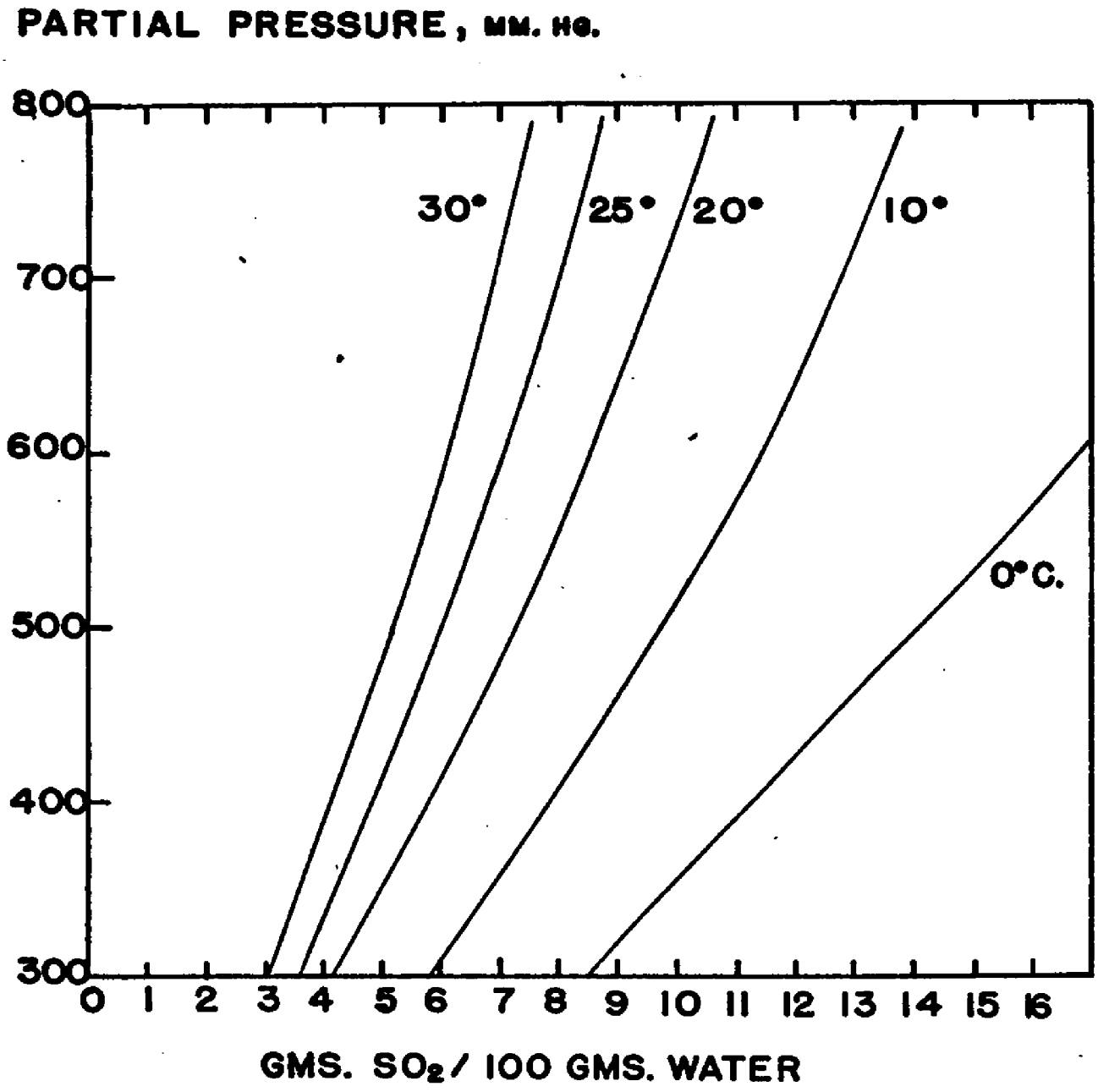

FIGURE 22, SOLUBILITY OF SULFUR DIOXIDE IN WATER

These two lines are plotted comparitively against the data obtained in this study from 14 runs at 25°C (see Figure 21). A total of 45 absorption rate observations were made over these 14 runs and the point averages are plotted. It is apparent that the higher values of the diffusion coefficient are erroneous and a value of D_{SO_2} closer to 1.8×10^{-5} $cm.^2/sec.$ is a better value. There is a literature value of 1.83×10^{-5}[8] which fits the data better. Since the laminar jet is a prime measurement of the diffusion coefficient, as explained by Himmelblau,[9] we can put some additional certainty in the value[10] of D_L as being 1.8×10^{-5} $cm.^2/sec.$ Additonal varification should be done, but since this was not the main purpose of the investigation, the work on SO_2 was used as another check before using the laminar jet technique on unknown systems, namely methyl mercaptan and water.

3. Methyl Mercaptan and Water

Methyl mercaptan data on solubility and diffusion coefficient is sparse or non-existant. In order to evaluate the mass transfer effects of methyl mercaptan in water, the solubility of the compound in water was measured at 25°C. This was done using a dynamic system, where the methyl mercaptan gas was bubbled through two gas scrubbers containing a known amount of water in a thermostated bath. Steady state was reached in less than 30 minutes. The liquid in each bottle was

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[8] D. W. Peaceman, "Liquid Side Resistant in Gas Absorption With and Without Chemical Reaction," (Sc.D. Thesis, Massachusetts Institute of Technology, 1951).

[9] D. M. Himmelblau, "Diffusion of Dissolved Gases in Liquids," Chemical Reviews, LXIV (1964), pp. 527-550.

[10] Ibid., p. 540.

titrated separately using iodometric technique. Correction for barometric pressure and water vapor pressure was applied, and the solubility calculated from the equivalent iodine consumed. The method was relatively precise (± .7%) and considered accurate enough for engineering data. The solubility of methyl mercaptan of 2.45×10^{-4} gm. mole/cc. was used in the calculation of the diffusion coefficient and mass transfer coefficient based on the penetration theory equations.

The experimental procedure for the absorption studies was essentially the same as used with the two previous systems described above, except for the obnoxious odors accompanying any accidental release. A system of gas collection and scrubbing using potassium permanganate solutions was effective in controlling emissions in the laboratory.

The result from the runs of methyl mercaptan in distilled water is tabulated in Appendix C. The data is plotted as the average absorption rate versus $1/\sqrt{t'}$ in Figure 23. The data can be correlated by a straight line through the origin, showing this system also follows the penetration theory. The maximum deviation occurs, as it did in the other two systems, at the lowest contact times. The equation for the straight line through the data is;

$$\bar{N}_A = 8.8 \times 10^{-7} \sqrt{\frac{1}{t'}} \qquad (6\text{-}4)$$

Since the proportionality term equals $2\ (C^*) \sqrt{\frac{D_{CH_3SH}}{\pi}}$, the diffusion

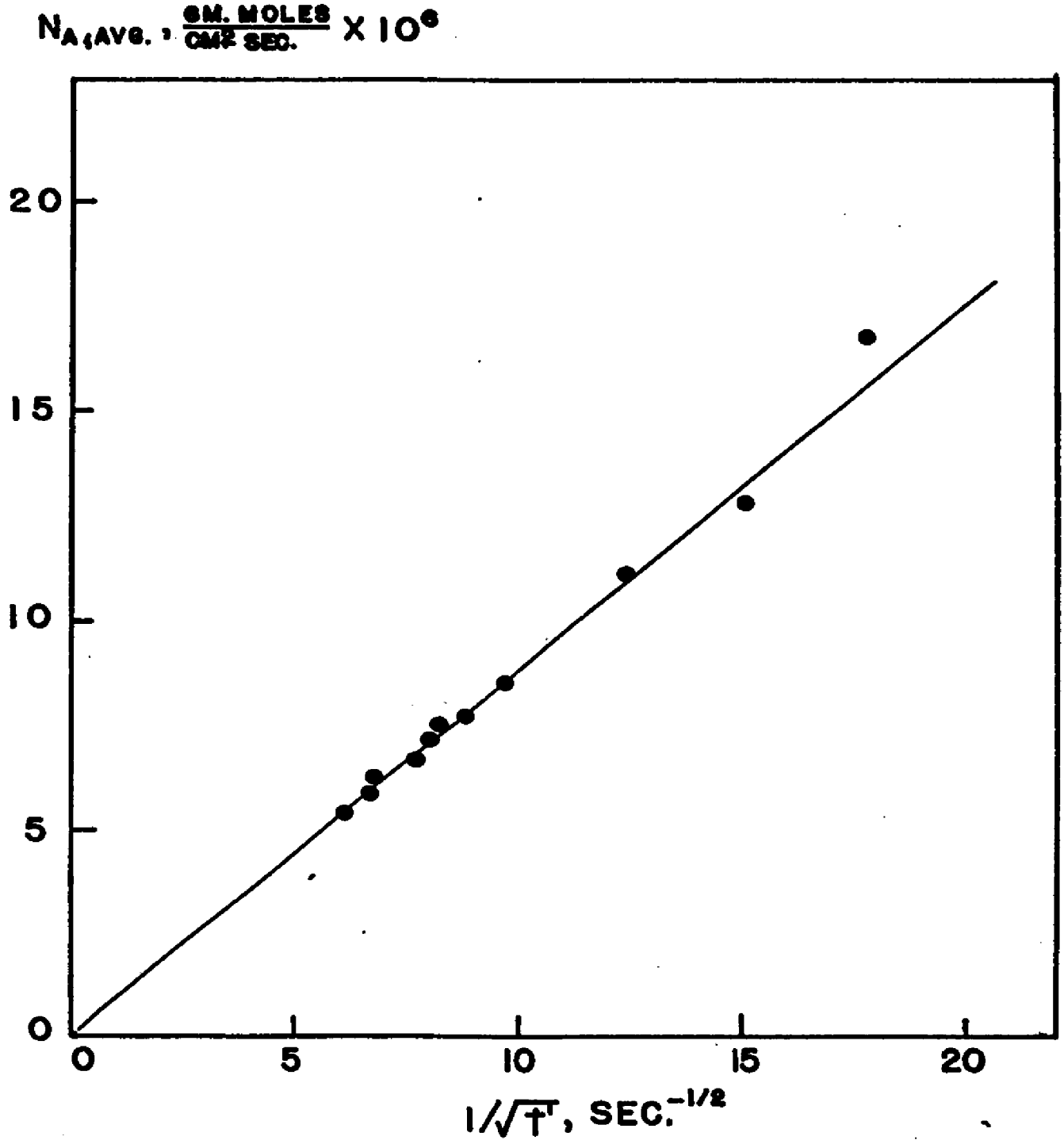

FIGURE 23, ABSORPTION OF METHYL MERCAPTAN IN WATER AT 25° C.

coefficient can be calculated. The coefficient is 1.03×10^{-5} cm.^{2}/sec. A prediction of the diffusion coefficient using the Wilke-Chang correlation gives $D = 1.53 \times 10^{-5}$ cm.^{2}/sec.,[11] not a bad comparison considering the correlation predicts D_L for H_2S as 1.9×10^{-5} versus the experimental value, 1.5×10^{-5} cm.^{2}/sec. Both of these compounds are slightly ionizing and have the common sulfide molecule, which may account for the failure of the prediction equations.

4. Methyl Mercaptan Absorption in Aqueous Sodium Hydroxide Solutions

For the system methyl mercaptan-aqueous sodium hydroxide solutions, a total of 48 runs at 6 sodium hydroxide levels were completed. The results of each run was converted into an absorption coefficient k_L (tabulated in Appendix D). The results are plotted in Figure 24 and compared to baseline coefficients for methyl mercaptan into water. The variable Φ was obtained by ratioing the k_L for chemical absorption, to the coefficient k_L^o for absorption without reaction (represented by the lowest line). The average of the Φ's along with the range calculated from this data are plotted versus the sodium hydroxide concentration in Figure 25. Note how the effect of reaction increases the absorption coefficient some twenty fold over the range studied.

a. Ionic Reaction

In Chapter III, Section 5, the postulated ionic reaction between the dissolved methyl mercaptan and the hydroxyl ion was described. Equation (3-23) showed;

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[11] The Othmer-Thakar correlation gives $D = 1.5 \times 10^{-5}$ cm.^{2}/sec.

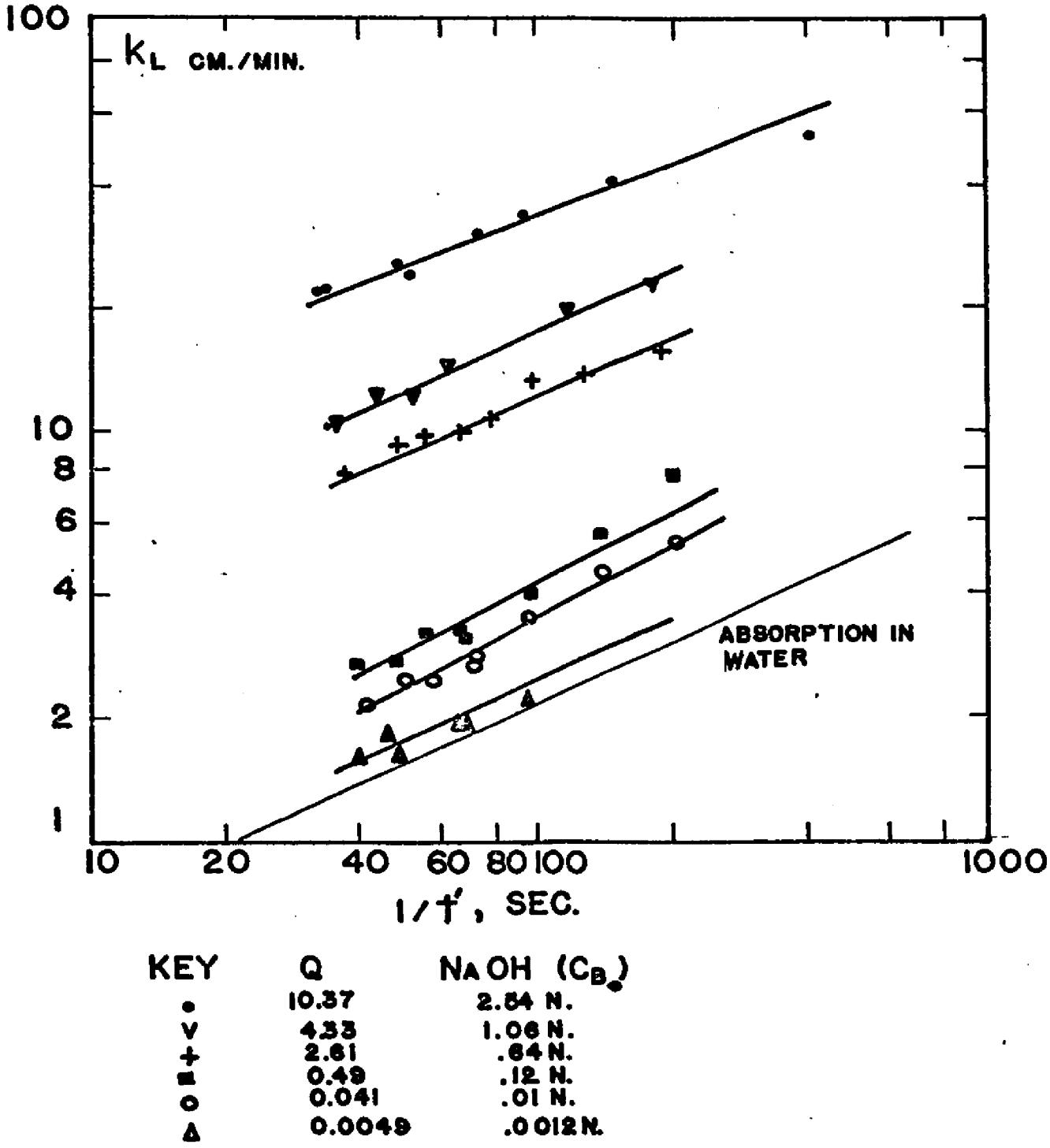

FIGURE 24, ABSORPTION COEFFICIENTS OF METHYL MERCAPTAN IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE.

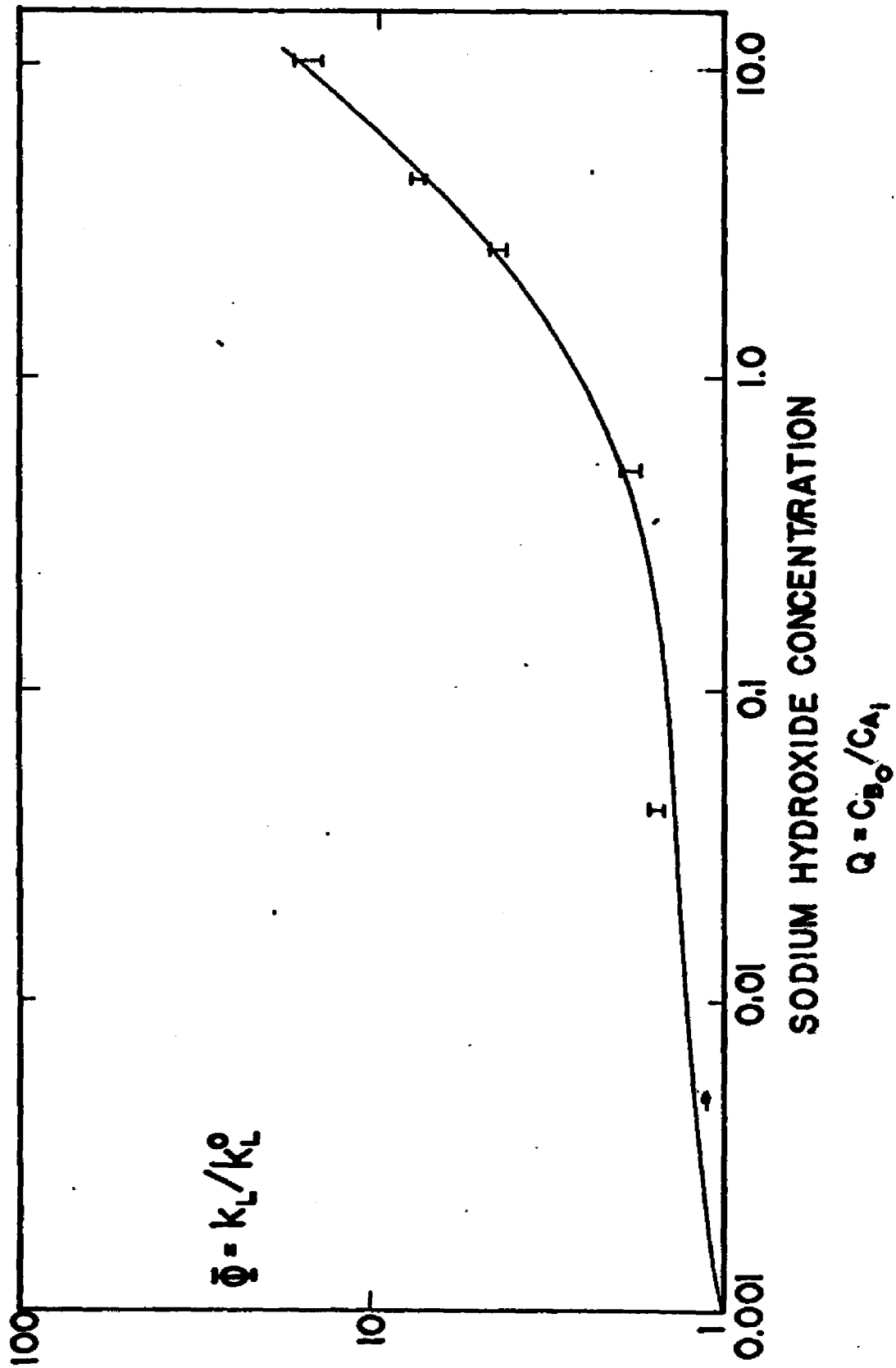

FIGURE 25 EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON ABSORPTION RATE.

$$CH_3SH_{(\ell)} + OH^-_{(\ell)} \rightarrow CH_3S^-_{(\ell)} + H_2O_{(\ell)} \qquad (3\text{-}23)$$

The stoichiometry is usually written to show a salt reacting with the weak acid to form another salt, sodium mercaptide. The mercaptide salt along with sodium hydroxide is completely ionized and Equation (3-23) showing the ionic species instead of the molecular salts represents the mechanism by which the exchange of a proton occurs. The exchange of a proton should be quite rapid. The frequency of collision of ions in solution is estimated from kinetic theory to be about 10^{11} liters/mole-sec.[12] According to the collision theory only a certain fraction of the collisions will result in a chemical combination (a proton exchange) since not all of the collisions will have the required activation energy. There may also be a steric factor, but it is not likely in this case. The above consideration should lead one to conclude that the reaction in Equation (3-23) would proceed quite rapidly and the data was tested to that effect.

Using the asymptotic solutions for the penetration theory described in Chapter V, Section 4, for absorption with an infinitely fast chemical reaction, the data was plotted comparatively. The theoretical solution is specified by the parameter r which is the ratio of the diffusivity of the solute gas over the diffusivity of the ionic liquid phase reactant. This value of r was evaluated using Equation (3-28) which considers the solute B to be the OH^- ion. The

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[12] M. Eigen, "Methods for Investigation of Ionic Reactions in Aqueous Solutions With Half-Times as Short as 10^{-9} Sec.," Discussions of the Faraday Society, XVII (1954), p. 194.

value of $r_{eff} = 2.91$. The variable Φ was correlated by the theoretical solution for infinitely fast reaction at the higher sodium hydroxide concentrations (see Figure 26). The ranges of Φ indicated in the ordinate direction may be due to error, but are more probably due to the effect of changing contact times on the absorption rate. The above analysis leads us to conclude that the rate of the postulated mechanism is very fast. However, further analysis yields an estimate of the rate of the forward reaction.

b. Estimate of the k_F, the Forward Reaction Rate Constant

An estimate of the reaction rate constant was obtained by applying the numerical solutions of Equations (3-29) and (3-30) for the specific r and q's which were studied. The result of the numerical solution for q = 10.37 and q = 4.33 are shown in Figure 27. The Φ's are specified by experimental data, as well as other parameters. The only unknown physical constant was k_F, which is a part of the variable plotted on the abscissa, M.

$$\sqrt{M} = \sqrt{\frac{k_F \, D_{CH_3SH} \, C_{B_o}}{k_L^o}} \qquad (3\text{-}32)$$

The plot was entered at the ordinate with values of Φ, and the values of M were read at the curve intercept. The values of k_F were calculated for each Φ and the results are tabulated in Table III. The best estimates are obtained for q = 10.37 because of the position from which the values are obtained on the curve. The values from the

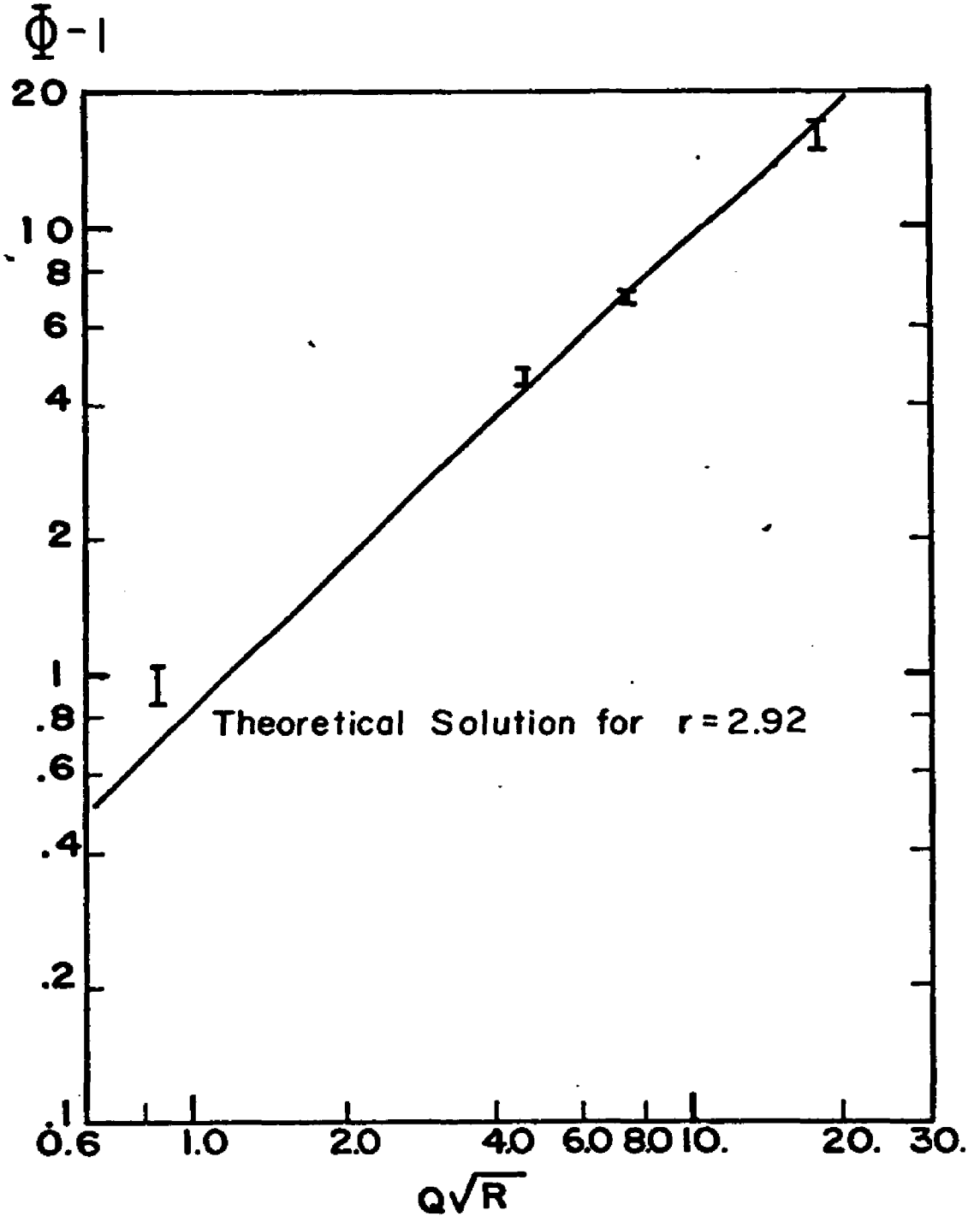

FIGURE 26, ABSORPTION RATE COMPARED WITH THEORETICAL SOLUTION FOR INFINITELY FAST SECOND ORDER REACTION.

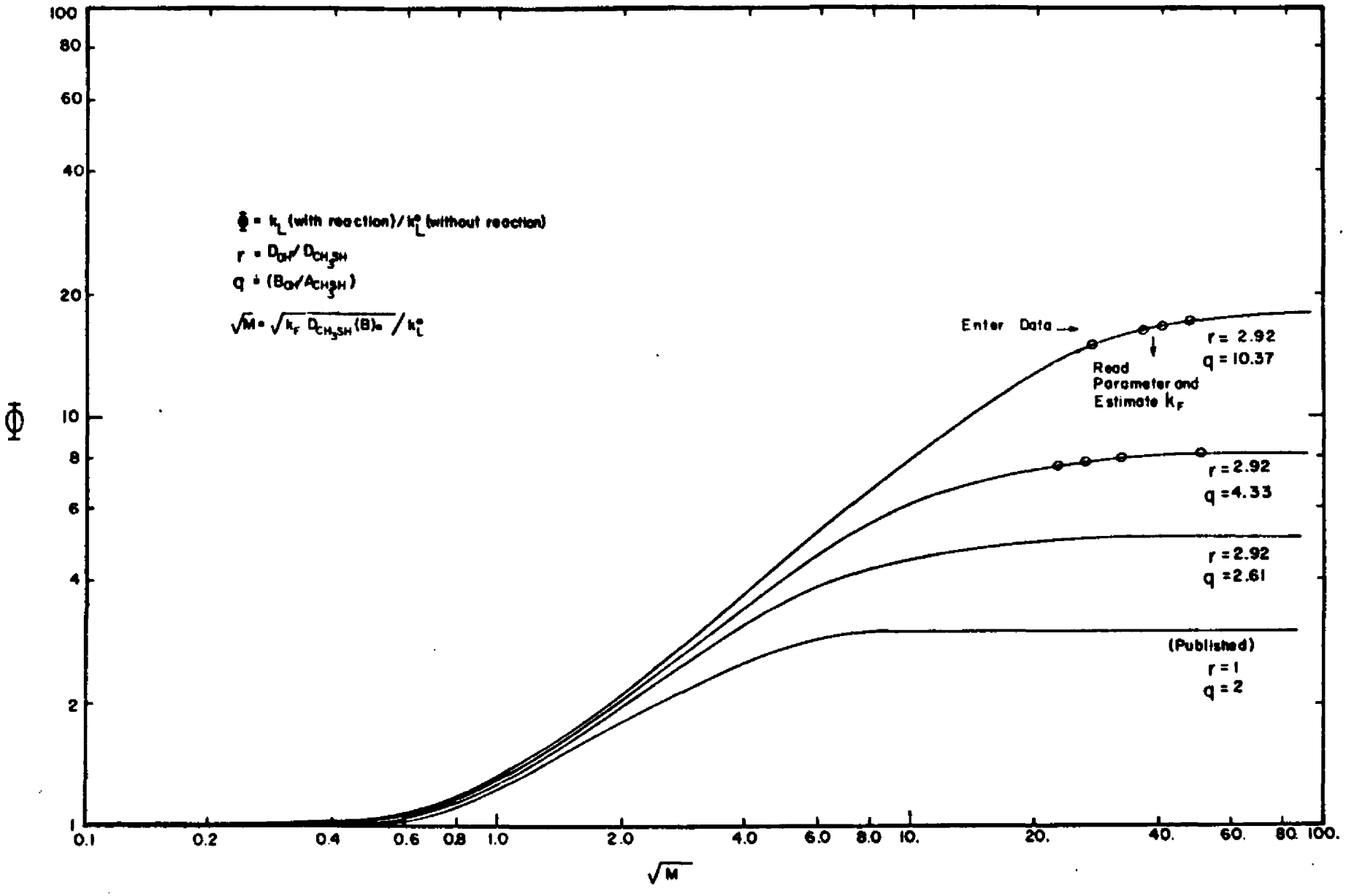

FIGURE 27, ESTIMATION OF FORWARD REACTION RATE CONSTANT

TABLE III

REACTIONS RATE CONSTANTS

q	k_L^o cm./min.	Φ	$\sqrt{M}$	k_F	
10.37	1.5	16.7	47.	5.3×10^4	$\frac{\text{liters}}{\text{gm.-mole-sec.}}$
	1.7	16.2	40.	5.1×10^4	"
	1.9	15.8	36.	5.0×10^4	"
	2.1	15.7	36.	6.1×10^4	"
	3.0	14.7	27.	7.0×10^4	"
			Avg.	5.6×10^4	@ 25°C
4.33	1.5	8.06	50.	13.9×10^4	"
	1.7	7.95	32.	7.8×10^4	"
	1.9	7.9	26.	6.2×10^4	"
	2.1	7.9	26.	7.6×10^4	"
	3.0	7.67	23.	12.0×10^4	"
			Avg.	9.5×10^4	

$$k_F = \frac{(\sqrt{M})^2 (k_L^o)^2}{(D_{CH_3SH})(C_{B_o})}$$

using; $C_{B_o} = .00254$ gm. moles/cc. at q = 10.37

$D_{CH_3SH} = 1.03$ cm.^{2}/sec.

second curve, q = 4.33 are taken from a near asymptotic section, and subject to reading errors. The results from this second curve are shown for comparison and are of the same order of magnitude, even if not nearly as constant. The value of k_F at 25°C is 5×10^4 liters/gm.-moles-sec., and in the range of ionic reaction rates. A crude estimate of the reaction rate between chlorine and sodium hydroxide obtained via another technique was given as 10^6 liters/gm.-mole-sec. (10^5 for CH_3SH - NaOH from this study as compared to 10^6 for Cl_2 - NaOH.

5. Extension of the Model to a Packed Absorber

A method of calculation for sizing packed absorbers was described in the previous chapter. These calculations were based on the application of the penetration theory to describe the effect of chemical reaction between methyl mercaptan and sodium hydroxide on the rate of absorption. The use of a multiplier, Φ, called an enhancement factor, in scaling the liquid phase coefficient, allows the evaluation of the overall resistance to absorption, or an overall coefficient, $K_G a$.

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{M}{\Phi k_L^o a} \qquad (6\text{-}5)$$

The factor, Φ, is a function of the reaction rate, concentration of the liquid phase solute and reactant, and the contact time of an element of fluid as described in the development of the theory. It can be evaluated easily in the limiting case where Φ is an asymptotic value, or more

difficultly in the intermediate case where the effect of reaction on diffusion is more nearly equal to the diffusion process. In the latter case the evaluation of Φ has been simplified by the use of empirical equations.

For extension of these concepts to a packed absorber, one of the difficulties is the evaluation of the contact time. The contact time is a distribution function, because there are contact surfaces of many different ages as the liquid is distributed over the packing in the absorber. This difficulty has been partly eliminated although the physical length of contact interval is still somewhat arbitrarily defined.

The data collected in the pilot absorber was represented as fraction absorbed versus the concentration of the sodium hydroxide in the liquid feed. Analyzing the plot of the data, it is evident that there are two limiting bounds on the absorption fraction: 1) with pure water where the liquid phase resistance is at a maximum and 2) at concentrated solutions of sodium hydroxide where there was no liquid resistance. From this data the gas phase mass transfer coefficient, the overall coefficient were calculated, and from that the liquid phase coefficient, was calculated. These were

$$k_G a = 8.8 \ \frac{\text{lb. mole}}{\text{hr. ft. (atm.)}}, \qquad H_G = .56 \text{ ft.} \tag{6-6}$$

$$k_L^o a = 35.4 \ \frac{\text{lb. mole}}{\text{hr. ft. (lb. mole/ft}^3\text{)}}, \quad H_L = 1.4 \text{ ft.} \tag{6-7}$$

The use of contact time in the penetration theory solution was eliminated by making use of the penetration theory definition of the liquid phase mass transfer coefficient.

$$k_L^o = 2 \sqrt{\frac{D}{\pi t'}} \tag{6-8}$$

or,

$$t' = \frac{4\pi}{D\ k_L^{o2}} \tag{6-8a}$$

This k_L^o is used in the definition of the parameter M, from which Φ can be evaluated, as follows

$$\theta \equiv k_F\ C_{B_o}\ t = \frac{4}{\pi} \left[\frac{k_F\ C_{B_o}\ D_A}{k_L^{o2}} \right] \equiv \frac{4}{\pi} [M] \tag{3-32}$$

and

$$\sqrt{M} = \sqrt{\frac{k_F\ C_{B_o}\ D_A}{k_L^o}}$$

In order to get a value of k_L^o, from the experimentally determined $k_L^o a$, the effective area of mass transfer was taken to be 50% of the total

area of the Intalox packing. Various correlations of effective areas of the different packings have been published. Correlations on Raschig rings show 22% to 40% effective area. Usually these effective areas are calculated from mass transfer data which measure absorption in stagnant and moving liquid elements. The use of this type of calculation can lead to errors when reaction is occurring, because absorption may occur equally effectively over the entire wetted area. The wetted area is almost always greater than the calculated effective area. The total area for 1/4" Intalox is around 300 $ft.^2/ft.^3$ based on extrapolations from data on Berl saddles, and other Intalox packing size. Lacking empirical correlations, and base data on total packing surface, the figure of 1/2 was arbitrarily chosen as the upper limit. In this system where the reaction rate is very fast, the use of smaller effective areas would give a longer contact time. The solution for the enhancement factor Φ is near the asymptotic region, so an error in the assumption of effective area does not greatly affect the final solution.

The evaluation of the forward reaction rate constant, k_F, for use in the parameter M, was described above. The diffusion coefficients of methyl mercaptan was measured as part of the absorption study with water, and the evaluation of the diffusion coefficient of hydroxyl ion as described in Appendix A.

The concentration of the hydroxyl ion in the liquid phase at various points of the column, was evaluated by means of a material balance considering the methyl mercaptan completely reacted.

Having these physical constants an enhancement factor, Φ, was calculated at the various increments in the column. The solutions was "cut and try" because the value of the interfacial concentration of dissolved solute could not be calculated until rate of mass transfer was determined.

Calculations on the packed tower was carried out on an I.B.M 7040 digital computer according to the method described in the previous chapter and the FORTRAN IV program which is included in Appendix G. The program was used to predict the change in absorption fraction and compared well with the data from the pilot absorber (see Figure 28). The method of calculation can be used to scale data from pilot absorbers and to size chemical absorbers with fast chemical reactions. The technique should be suitable for intermediate reactions providing some basic data is measured or can be predicted.

The liquid phase and gas phase, height of transfer units were calculated for the pilot absorber using published correlations for the specific tower packing and flow characteristics. The H_G for this system was calculated to be 0.55 ft. based on work with a highly soluble system.[13] Extrapolating another correlation[14] based on the absorption of methanol in water for 15 mm. Raschig rings, predicts H_G to be 0.7 ft. The experimental data on the packed absorber indicated the height of a transfer unit (H_G) in the case of gas phase

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[13] J. H. Perry, Chemical Engineers' Handbook, (4th Edition; New York: McGraw-Hill, Inc., 1963), 14-19.

[14] F. Yoshida and T. Koyanagi, "Mass Transfer and Effective Interfacial Areas in Packed Columns," A.I.Ch.E. Journal, III (1962), p. 309.

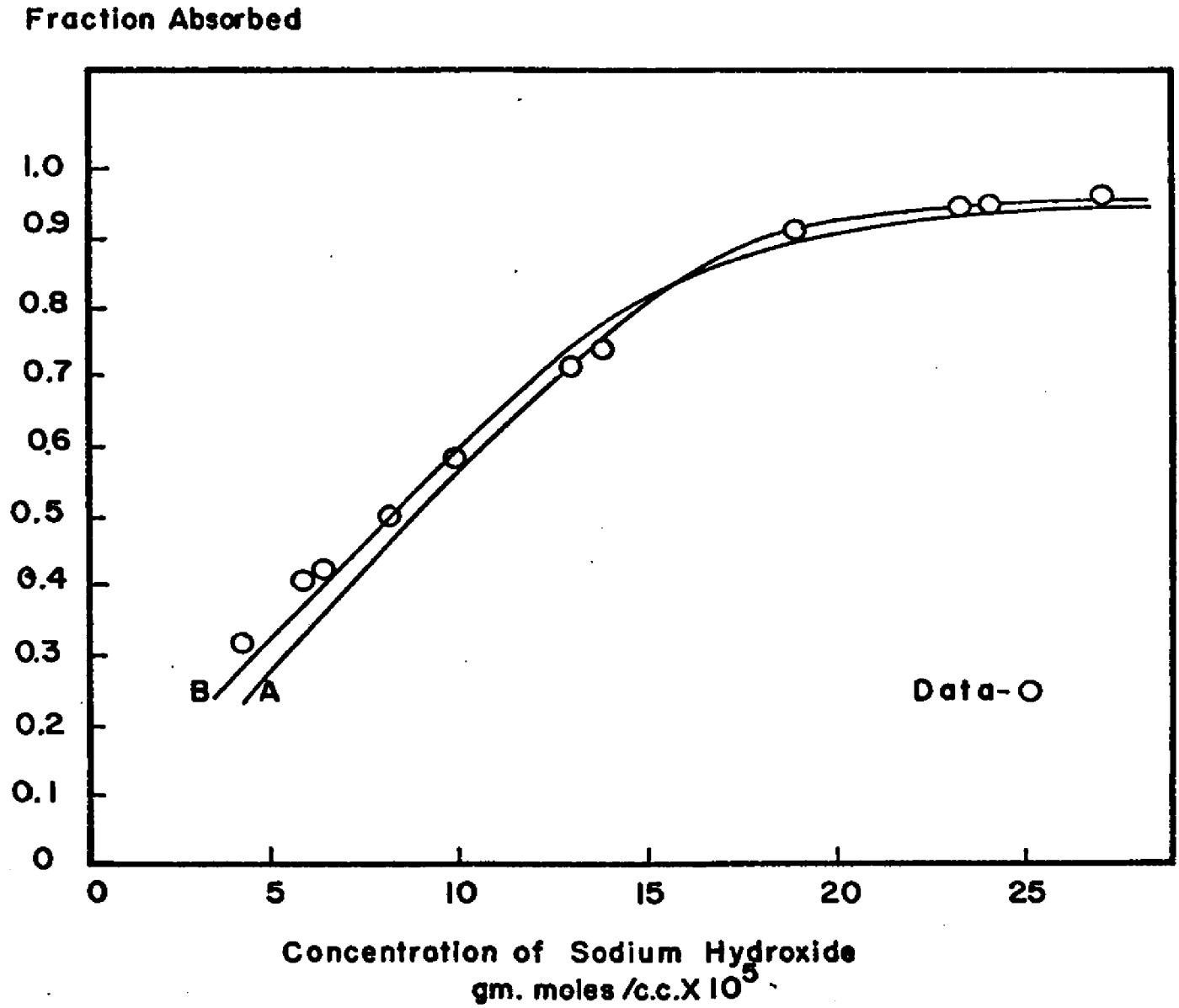

Figure 28, Theoretical Solutions for Packed Absorber

A – Solubility, 67 atm./(lb. mol./ft.^{3})
B – Solubility, 100atm./(lb. mol./ft.^{3})

limiting was 0.56 ft. This compares best with the correlation of reference 13, where the highly soluble system was ammonia and water which can be classed as chamical absorption. The absorption of methyl mercaptan into sodium hydroxide at high concentrations is a highly soluble system. Equipment sizing for similar systems with different packing geometries and flow rates should be based on these gas phase coefficient correlations.

The liquid phase height of a transfer unit, H_L, was estimated[15] to be 1.2 ft. for the absorption of methyl mercaptan in water. Calculations of the experimental value of H_L gives 1.4 ft. for the pilot tower. The experimental value is higher but probably within the accuracy of the correlation. Again these correlations seem suitable for predicting the mass transfer coefficients useful in the sizing of larger equipment. The effect of reaction on the liquid phase coefficient can be calculated as described above.

A design technique is proposed for sizing packed towers for absorption accompanied by a rapid second order chemical reaction. The method outline is;

1) evaluate or estimate the reaction rate constant at the operating temperature. Operating temperatures are normally near ambient conditions because of the effect on solubility.

2) estimate the diffusion coefficients of the solute gas and the liquid phase reactant, taking into account the fact that the ionic species may be the main diffusing component.

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[15] Ibid.

3) estimate the individual gas and liquid phase mass transfer coefficients for the specific column characteristics and flow rates.

4) evaluate the enhancement parameter Φ using the correlation for the second order mechanism described in the text, of Chapter V.

5) calculate the tower height for the specified fraction absorption and inlet feed concentrations of gas and liquid components.

6) increase liquid feed concentration until tower height does not decrease further. This is the gas phase limiting condition. Allow additional liquid feed for operating variations.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Based on experimental and theoretical results, the following conclusions and recommendations are offered:

(a) The gas absorption rates measured by the laminar liquid jet apparatus are predicted by the penetration theory results for the cases of physical absorption and absorption with chemical reaction. The flow of the liquid jet discharged from a diaphragm orifice is laminar and matches the boundary conditions used in the penetration theory solutions.

(b) The laminar liquid jet is very well suited for measuring diffusion coefficients and absorption coefficients in liquids. The accuracy of the technique is ± 5%.

(c) The correlations for prediction of liquid diffusion coefficients of methyl mercaptan in water give values which are considerably different from the experimentally measured values.

(d) The published mathematical solutions of the penetration theory for gas absorption accompanied by a second order chemical reaction can be used to infer reaction mechanisms.

(e) The mechanism for reaction of methyl mercaptan with aqueous sodium hydroxide in the concentration range of 0.12 N. to 2.5 N. is represented by the following equation.

$$CH_3SH_{(\ell)} + OH^-_{(\ell)} \rightarrow CH_3S^-_{(\ell)} + HOH_{(\ell)}$$

The diffusion of the ions (instead of the molecular species) are important in determining the rate of the mass transfer process.

(f) The forward reaction rate constant of the reaction postulated above is very large and in the range of ionic reactions.

(g) The mass transfer process can be adequately described by the solutions for an infinitely fast second order irreversible chemical reaction.

(h) The empirical correlation for the enhancement factor Φ was found to be adequate in predicting numerical values for a second order reaction without relying on a numerical solution for one of the parameters; the Φ_a for a pseudo-second order reaction. The substitution of the analytical solution for Φ_a for the pseudo-first order case in place of the Φ_a (second-order) allowed for a rapid computer calculation of $\Phi_{q,\ 2nd\ order}$.

(i) The extension of the laboratory data and the description of gas absorption in a packed absorber for the methyl mercaptan-

sodium hydroxide system can be made using solutions of the penetration theory in a technique developed in this work.

(j) The results obtained in the series of steps used in the development of this study justify further work in this area. The design technique is general and will work on absorption with chemical reactions of intermediate rates; slower than ionic reactions. Such studies could be used in further tests of the published mathematical solutions for the penetration theory with chemical reaction. The comparison of known reaction rate constants obtained by other techniques to the determinations made by the laminar jet would make a valid contribution.

(k) The following recommendations are offered to extend this study.

(1) use the design technique to scale-up a packed absorber.

(2) use the data from this study to design agitated gas liquid contactors operating on the same system, and develop design criteria based new or current mathematical theories for agitated gas liquid contactors.

(3) study the effect of catalysis on the reaction rates.

(4) use the apparatus to measure diffusion coefficients in systems where research has been thwarted because of analytical difficulties. The laminar liquid jet does not require chemical analysis when operating with a pure gas stream.

(5) use the apparatus to measure multicomponent absorption when analytical methods are available such as gas chromatographic analysis which can be used in organic absorption systems.

Notation

$a = C_A/C_{A_i}$.

$b = C_{B_o}/C_B$.

C_A = concentration of species A in liquid phase, moles/cc.

C_{A_i} = concentration of species A at liquid interface.

C_B = concentration of species B in liquid phase, moles/cc.

C_{B_o} = concentration of species B at the start of a contact time interval.

C_i = concentration of a species at liquid interface, moles/cc.

C^* = concentration of solute gas in liquid which would be in equilibrium with gas, mole/cc.

C_L = concentration of solute gas in bulk of liquid, moles/cc.

D_A, D_B, D_I = diffusivity of species A, B, and ions respectively in liquid sq. cm./sec.

D_L = diffusivity of solute gas in liquid, sq. cm./sec.

D_{AB}^t = eddy diffusivity of species A through phase B in turbulent flow, sq. cm./sec.

D_V = volumetric diffusivity, sq. cm./sec.

D = diameter, cm.

D_o = orifice diameter, or initial diameter of laminar liquid jet, cm.

D = electric field, V./cm.

F = Faraday constant = 96,500 coulombs/g. equiv.

G = superficial gas flow through packed tower, lbs./ft.^{2}-hr.

g = acceleration due to gravity, cm./sec.^{2}

h_S, h_I, h_P = height of packed section in surface reaction zone, interior reactor zone, and physical absorption zone respectively, ft.

$[I]$ = concentration of species I in the aqueous phase, g-ions/cc.

J_A = flux of mass, moles/cm.^{2}-sec.

J_q = flux of heat, cal./cm.^{2}-sec.

J^t = flux of mass in turbulent flow, moles/cm.^{2}-sec.

k = Boltzmann constant, or thermal conductivity in Equation (3-1), cal.

k_L^o = liquid phase absorption coefficient, physical absorption with no chemical reaction cm./sec. or m usual units gm.mole/cm.^{2}-sec. $(\frac{\text{gm. mole}}{\text{cc.}})$.

k_L = liquid phase absorption coefficient, cm./sec. based on average absorption rate for penetration theory, cm./sec.

k_La = liquid phase absorption coefficient used in packed towers where area is unknown, lb.mole/hr. ft.^{3} (lb. mole / ft.^{3}) or, 1/hr.

K_La = overall liquid phase absorption coefficient, considering the effect of chemical reaction, 1/hr.

K_L^oa = overall liquid phase absorption coefficient, 1/hr., for physical absorption with no chemical reaction.

k_g = gas phase absorption coefficient, based on film theory, lbm./hr. ft.^{2} (atm.).

k_ga = gas phase absorption coefficient used in packed towers where transfer area is unknown, lb. mole/hr. ft.^{3} (atm.).

k_F = forward reaction rate constant, cc./(mole)(sec.).

L = superficial liquid flow rate, lbs./hr.-ft.^{2}

L_M = metal superficial liquid flow rate, lb. moles/hr. ft.^{2}

$M = k_F D_A B_o/(k_L^o)^2$ in general

$= (\pi/4)\ \theta$ for penetration theory.

M_B = molecular weight of species B.

m = mass of molecule in Equation (3-4), f.f., and solubility of solute species in liquid, from Henry's Law, atm./(lb. mole/ft.^{3}).

N = no. of molecules.

$\tilde{N}$ = Avogadro's number.

N_A = average absorption rate, gm.-moles/cm.^{2}-sec.

N_l = local flux of ionic species in Equation (3-26).

P = system pressure, atm.

p_G = partial pressure of solute component in bulk gas stream, atm.

p^* = partial pressure of solute gas in gas phase which would be in equilibrium with liquid, atm.

$q = C_{B_o}/C_{A_i}$.

q' = volumetric flow rate in Equation (5-1), cc./sec.

$r = D_B/D_A$, evaluated as an effective ratio for diffusion of ionic species by Equation (3-27).

R = gas law constant.

$R_A = D_{OH^-}/D_{CH_3SH}$.

S = Danckwerts' distribution factor.

t = time, sec.

t' = temperature, ^oK.

$\tilde{V}_A$ = molal volume, cc./mole.

$\tilde{v}$ = mean molecular velocity, cm./sec.

x = distance into liquid phase, cm.

y = distance down the laminar liquid jet, cm.

y_n, y_1, y_2, = mole fraction of A in the bulk gas stream with subscript $n = 1, 2, 3 \ldots$ the position index.

Z_l = valence of species l.

$$Z = \sqrt{\frac{k_F B_o}{D_A}}\ (\chi) \ .$$

Greek Letters

α = constants defined where used.

β = constant defined where used.

γ = constant defined where used.

$\Phi = k_L / k_L^o$.

Φ_a = asymptotic value of Φ at large values of θ (or $\sqrt{M}$).

ψ_B = association parameter used in diffusion correlation by Wilke.

χ = variable substituted in solution of Equation (5-4).

η = dimensionless length variable $= \dfrac{X}{\sqrt{4\ D_A\ t}}$.

$\theta = K_F\ C_{B_o}\ t$, dimensionless time of contact.

$\Psi = \chi$; first derivative of χ with respect to η .

μ = viscosity, centipoise.

K = Boltzman's constant.

λ_1 = mean free path.

Ω_o = collision integral.

σ_{AB} = collision diameter.

σ = parameter in parametric equations.

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APPENDICES

APPENDIX A

CALCULATION OF IONIC DIFFUSIVITIES

In the case of gas absorption with simultaneous ionic reactions, it is the diffusion of the ionic specie that is important, and allowance must be made for the fact that the individual ions in the presence of other ions may diffuse at rates which are different from those of their original molecular specie pair. Sherwood and Wei[1] showed how the results of Vinograd and McBain[2] could be extended to irreversible reactions by estimating the concentration gradients. The Hatta film theory may be used to graphically depict the diffusion of methyl mercaptan into the aqueous sodium hydroxide solution, followed by a reaction to form the salt (see Figure 2).

$$CH_3SH_{(g)} \rightleftarrows CH_3SH_{(\ell)} \qquad \text{(A.A-1)}$$

$$CH_3SH_{(\ell)} \rightleftarrows CH_3S^- + H^+ \qquad \text{(A.A-2)}$$

$$NaOH_{(\ell)} \rightarrow Na^+_{(\ell)} + OH^-_{(\ell)} \qquad \text{(A.A-3)}$$

$$CH_3SH_{(\ell)} + Na^+_{(\ell)} + OH^-_{(\ell)} \rightarrow CH_3S^-_{(\ell)} + Na^+_{(\ell)} + HOH_{(\ell)} \qquad \text{(A.A-4)}$$

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[1] T. K. Sherwood and J. C. Wei, "Ion Diffusion in Mass Transfer Between Phases," A.I.Ch.E. Journal, I (1955), p. 522.

[2] J. R. Vinograd and J. W. McBain, "Diffusion of Electrolytes and of the Ions in Their Mixtures," Journal of the American Chemical Society, LXII (1961), p. 2008.

Vinograd and McBain, following the Nernst theory, wrote diffusion equations for each ion. The authors imposed the conditions of electrical neutrality at each point and linear concentration gradients. The following equation was derived for the diffusion of cations:

$$n_+N_+ = -\frac{RT}{F}\frac{U_+}{n_+}\left(G_+ - n_+C_+\frac{\Sigma U_+G_+/n_+ - \Sigma U_-G_-/n_-}{\Sigma U_+C_+ + \Sigma U_+C_-}\right) \qquad \text{(A.A-5)}$$

Here N_+ is the ion flux of a particular cation having a valence n_+, concentration C_+, and mobility U_+; G_+ is the concentration gradient dC_+/dx of this cation in the direction of diffusion, and the minus signs refer to the anions. The derivation is subjected to the limitation that the activity coefficients and collision effects are ignored, as are the effects of ion pairs or ionic complexes. All of these approximations are well within the accuracy of the analysis of mass transfer effect.

Sherwood and Ryan[3] have given the solution in closed form as,

$$r_{eff} \equiv \frac{2R_A}{1 + \sqrt{B\left(\frac{R_A}{R_P} - 1\right) + 1}} \qquad \text{(A.A-6)}$$

where $R_A = D_{OH^-}/D_{CH_3SH}$

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[3] T. K. Sherwood and J. M. Ryan, "Mass Transfer to a Turbulent Fluid With and Without Chemical Reaction," Chemical Engineering Science, XI (1959), p. 81.

$$R_p = D_{CH_3S^-}/D_{CH_3SH}$$

$$B = [OH^-]_o/[Na^+]_o$$

The values of these diffusion coefficients were all known except the diffusion of the mercaptide ion CH_3S^-. Other investigators have reported values for the diffusion coefficient of the acetate ion, which is approximately the same size and has the same charge as the mercaptide ion. As the nearest approximation, the two were ratioed according the molecular weight and the value used for the diffusion of the mercaptide ion. The values of the variables in Equation (A.A-6) are

$D_{CH_3S^-} = 1.0$ cm.^{2}/day $\qquad R_A = D_{OH^-}/D_{CH_3SH} = 4.4$

$C_{CH_3SH} = 1.03$ cm.^{2}/day $\qquad R_p = D_{CH_3S^-}/D_{CH_3SH} = .97$

$D_{OH^-} = 4.54$ cm.^{2}/day

$B = 1$

$$r_{eff} = \frac{(2)(4.4)}{1 + \sqrt{(1)(4.4/.97-1) + 1}} = 2.91$$

APPENDIX B

CARBON DIOXIDE AND WATER DATA

Operating Conditions

Barometric Pressure 30.18 in. Hg.

Room Temperature 26°C

Liquid Temperature 25.5°C

Run	Jet Length (cm.)	Liquid Rotameter Reading	Liquid Rotameter Flow Rate (cc./sec.)	Average Gas Absorption Rate (cc./sec.)	No. of Observations
1	3.441	6	2.55	0.0490	6
2	3.441	8	3.60	0.0571	8
3	5.606	6	2.55	0.0619	5
4	5.606	8	3.60	0.0724	5
5	1.476	6	2.55	0.0348	5
6	1.476	8	3.60	0.0413	5
7	6.941	6	2.55	0.0670	5
8	6.941	8	3.60	0.0778	5
9	8.026	6	2.55	0.0670	3
10	8.026	8	3.60	0.0782	5
11	1.056	6	2.55	0.0255	3
12	1.056	8	3.60	0.0329	3
13	4.281	6	2.55	0.0490	4
14	4.281	8	3.60	0.0582	4

APPENDIX B (Continued)

SULFUR DIOXIDE AND WATER DATA

Operating Conditions

Barometric Pressure 30.05 in. Hg.

Room Temperature 26.5°C

Liquid Temperature 25°C

Run	Jet Length (cm.)	Liquid Rotameter Reading	Liquid Rotameter Flow Rate (cc./sec.)	Average Gas Absorption Rate (cc./sec.)	No. of Observations
1	8.33	5	1.92	2.1	5
2	8.33	6	2.55	2.06	5
3	7.736	6	2.55	2.08	5
4	7.736	6	2.55	2.31	3
5	5.730	6	2.55	2.00	5
6	7.736	8	3.60	2.62	4
7	7.736	8	3.60	2.44	4
8	4.94	6	2.55	1.65	3
9	4.94	8	3.60	2.04	5
10	4.77	8	3.60	1.85	3
11	1.416	8	3.60	1.11	3
12	.95	6	2.55	0.763	5
13	.95	8	3.60	0.91	4

APPENDIX C

METHYL MERCAPTAN AND WATER DATA

Operating Conditions

Barometric Pressure 30.10 in. Hg.

Room Temperature 26°C

Liquid Temperature 25.0°C

Run	Jet Length (cm.)	Liquid Rotameter Reading	Liquid Rotameter Flow Rate (cc./sec.)	Average Gas Absorption Rate (cc./sec.)	No. of Observations
1	4.341	6.	2.55	0.0574	7
2	4.341	8.	3.60	0.0727	5
3	7.416	8.	3.60	0.1602	4
4	7.416	9.	4.17	0.1789	5
5	2.226	6.	2.55	0.1199	11
6	2.226	8.	3.60	0.2232	5
7	3.771	6.	2.55	0.2528	5
8	3.771	8.	3.60	0.2847	7
9	5.421	6.	2.55	0.2998	8
10	5.421	8,	3.60	0.3407	6
11	5.421	9.	4.17	0.3641	4
12	6.836	6.	2.55	0.3216	5
13	6.836	8.	3.60	0.3760	4
14	6.836	9.	4.17	0.3967	5
15	1.106	6.	2.55	0.1279	3
16	1.106	8.	3.60	0.1656	4

APPENDIX D

METHYL MERCAPTAN AND SODIUM HYDROXIDE ABSORPTION DATA

Run	NaOH Conc. Normal	Liquid Flow Rate (cc./sec.)	Height (cm.)	Average Absorption Rate (cc./sec.)	No. of Observations
101	0.0012	2.55	1.891	0.1315	6
102			3.646	0.255	8
103			5.156	0.305	8
104			6.216	0.362	7
105		3.60	1.891	0.144	7
106			3.646	0.291	7
107			5.156	0.351	6
108			6.216	0.421	6
109	0.01	2.55	1.736	0.291	9
110			3.496	0.353	7
111			5.041	0.456	7
112			6.111	0.461	8
113		3.60	1.736	0.338	8
114			3.496	0.447	9
115			5.041	0.480	7
116			6.111	0.531	5
117	0.12	2.48	1.736	0.351	5
118			3.466	0.408	4
119			5.006	0.489	5
120			6.136	0.590	4
121		3.49	1.736	0.416	6
122			3.466	0.477	4
123			5.006	0.557	5
124			6.136	0.700	6
125	.64	2.38	1.766	0.868	5
126			3.496	1.248	5
127			5.026	1.620	6
128			6.136	1.700	7
129		3.42	1.766	0.980	5
130			3.496	1.627	5
131			5.026	1.798	5
132			6.136	2.100	7
133	1.06	2.23	1.786	1.245	5

APPENDIX D (Continued)

METHYL MERCAPTAN AND SODIUM HYDROXIDE ABSORPTION DATA

Run	NaOH Conc. Normal	Liquid Flow Rate (cc./sec.)	Height (cm.)	Average Absorption Rate (cc./sec.)	No. of Observations
134			3.461	1.280	5
135			5.006	2.154	4
136			6.111	2.320	5
137		3.24	1.786	1.462	5
138			3.461	1.500	4
139			5.006	2.57	3
140			6.111	2.60	5
141	2.54	1.7	0.786	1.154	5
142			1.711	2.110	7
143			3.456	3.200	4
144			5.006	3.930	8
145		2.58	0.786	1.482	5
146			1.711	2.560	5
147			3.456	3.730	6
148			5.006	4.180	7

APPENDIX D (Continued)

CALCULATION OF MASS TRANSFER COEFFICIENTS

Run	Area $Cm.^2$	$1/\theta$ $sec.^{-1}$	Flux, N/A $cm.^3/cm.^2$-sec. $\times 10^2$	k_L cm./min.
101	0.695	125.3	18.9	1.91
102	1.33	66.1	19.2	1.95
103	1.86	47.6	16.4	1.66
104	2.24	39.6	16.2	1.64
105	0.68	182.0	21.1	2.14
106	1.32	90.8	22.1	2.24
107	1.86	67.7	18.9	1.91
108	2.24	55.9	18.8	1.90
109	0.64	136.0	45.5	4.60
110	1.28	69.0	27.6	2.80
111	1.82	48.7	25.1	2.54
112	2.20	40.5	21.0	2.13
113	0.63	199.0	53.9	5.45
114	1.26	91.0	35.3	3.57
115	1.82	69.0	26.4	2.68
116	2.20	57.0	24.2	2.45
117	0.64	134.5	55.1	5.58
118	1.26	67.7	32.3	3.27
119	1.80	47.7	27.1	2.74
120	2.20	39.7	26.8	2.74
121	0.62	135.0	65.0	6.74
122	1.25	97.0	38.2	3.87
123	1.81	67.3	30.8	3.12
124	2.21	54.7	31.6	3.20
125	0.648	125.0	13.4	1.36
126	1.27	65.3	9.8	9.95
127	1.81	45.5	8.9	9.10
128	2.21	37.4	7.7	7.80
129	0.639	185.0	15.3	15.5
130	1.25	96.0	13.0	13.2
131	1.80	66.5	10.0	10.1
132	2.19	55.0	9.6	9.7
133	0.66	116.5	19.0	19.3

APPENDIX D (Continued)

CALCULATION OF MASS TRANSFER COEFFICIENTS

Run	Area $Cm.^2$	$1/\theta$ $sec.^{-1}$	Flux, N/A $cm.^3/cm.^2$-sec. $\times 10^2$	k_L cm./min.
135	1.81	43.3	11.9	12.1
136	2.20	35.3	10.6	10.7
137	0.64	174.0	22.6	22.9
139	1.79	63.3	14.3	14.6
140	2.19	52.0	11.8	12.0
141	0.292	92.0	33.5	33.9
142	0.630	46.5	25.4	25.7
143	1.26	32.5	21.7	22.0
145	0.292	300.0	50.7	51.4
146	0.630	141.0	40.6	41.1
147	1.26	70.5	29.6	30.0
148	1.81	57.4	23.0	23.3

APPENDIX D (Continued)

EFFECT OF HYDROXYL CONCENTRATION ON ABSORPTION COEFFICIENT

q	.0049		0.041		0.49		2.61		4.33		10.37	
k_L^o	k_L	Φ	k_L	Φ	k_L	Φ	k_L	Φ	k_L	Φ	k_L	Φ
1.5	1.7	1.13	2.3	1.53	2.8	1.86	8.7	5.8	12.1	8.06	25.0	16.7
1.7	1.9	1.12	2.65	1.56	3.2	1.88	9.6	5.65	13.5	7.95	27.5	16.2
1.9	2.15	1.13	3.0	1.58	3.7	1.95	10.6	5.58	15.0	7.9	30.0	15.8
2.1	2.35	1.12	3.35	1.59	4.1	1.95	11.7	5.57	16.6	7.9	33.0	15.7
3.0	3.4	1.13	5.10	1.70	6.2	2.07	16.2	5.4	23.0	7.67	44.0	14.7

APPENDIX E

EVALUATION OF THE PARAMETER Φ FROM THE EMPIRICAL CORRELATIVE EQUATION

The results of the numerical solutions of the penetration theory equations for absorption accompanied by chemical reaction can be correlated by a simple expression.

$$\left[\frac{(\sqrt{M})_q}{(\sqrt{M})}\ \text{pseudo nth order}\right]_{\text{same }\Phi} = \left(\frac{\Phi_a - 1}{\Phi_a - \Phi}\right)^{\gamma} \qquad \text{(A.E-1)}$$

where $\gamma = .4m$ for $1 \leq m \leq 3$

$\gamma = .23$ for $m = .5$

The correlation equation is most readily used by solving for $\sqrt{M}$ at a given value of Φ using the published plots of Φ_a. The utility of this equation in high speed design computations depends on the representation of Φ_a by a mathematical expression. Even then the solution requires an iterative technique. This was done by the "method of successive approximations" and is described below.

Solving Equation (A.E-1) for Φ, one obtains;

$$\Phi = \Phi_a - \frac{\Phi_a - 1}{\left[\dfrac{(\sqrt{M})_{2,q}}{(\sqrt{M})\ \text{pseudo 2nd order}}\right]^{2.5}_{\text{same }\Phi}} \qquad \text{(A.E-2)}$$

for a second order chemical reaction.

The analytical equation found to represent Φ_a accurately enough (with a maximum error of 1%) is,

$$\Phi = \sqrt{M}\left[1 + \frac{\pi}{8M}\right] \operatorname{erf}\sqrt{\frac{4M}{\pi}} + \tfrac{1}{2} \exp\left(\frac{-4M}{\pi}\right) \qquad \text{(A.E-3)}$$

It is the exact solution for a pseudo first order and used in this case because the order of the reaction in pseudo cases does not affect the solution. A maximum deviation of 3% between zero order and third order; as accurate as picking values from the small plots which have been published.

Solving Equation (A.E-3) explicitly of M (or $\sqrt{M}$) is not practical, therefore the parameter is expressed as a function of itself for the iterative method of solution as follows,

$$(\sqrt{M})_{i+1} = \frac{\Phi - \pi/8\sqrt{M_i} \operatorname{erf}\sqrt{\frac{4M_i}{\pi}} + \tfrac{1}{2} \exp\left(\frac{-4M_i}{\pi}\right)}{\operatorname{erf}\sqrt{\frac{4M_i}{\pi}}} \qquad \text{(A.E-4)}$$

The calculation procedure starts with having a value of $(\sqrt{M})_{2,q}$ and desiring a value of Φ. Entering Equation (A.E-2) with values of $(\sqrt{M})_{2,q}$ $\Phi_a \cong 1 + \sqrt{rq}$, and an estimate of $(\sqrt{M})$ pseudo 2nd order, a value of Φ is obtained. This Φ and the first estimate of M $(\sqrt{M_i})$ is used to get a new estimate of M $(\sqrt{M_{i+1}})$ from Equation (A.E-4). The late value of M is used again in Equation (A.E-2) to get another Φ,

and Equation (A.E-4) to get a late value of M ($\sqrt{M}_{i+1}$). This is used successively until a convergence test on the value of $\sqrt{M}$ is met, as shown in the following FORTRAN program. The two equations could be combined to eliminate Φ, but since Φ is a desired result, there was no need to destroy its identity and have to recalculate it. Table A.E-1 shows how test runs proved the validity of the method which was used as a subroutine in a larger program.

FORTRAN IV PROGRAM FOR TESTING EMPIRICAL CORRELATION

```
      DIMENSION SMS(900)
99    READ 111,SM,T
      Q=2.0
      R=1.0
      PHIA=1.+Q*SQRT(R)
      SMS(1)=SM
100   I=I+1
      PHI=PHIA-(PHIA-1.)/(SM/SMS(I))**2.5
      SMS(I+1)=(PHI-3.14/(8.*SMS(I))*ERF(1.129*SMS(I))+
     1.5*EXP(-1.274*SMS(I)**2))/ERF(1.129*SMS(I))
      TA=ABS(SMS(I+1)-SMS(I))
      IF(T-TA) 100,100,101
101   PRINT 112,SM,PHI,I
      GO TO 99
111   FORMAT (2F10.5)
112   FORMAT(1X,2F20.5,I4)
      END
```

TYPICAL OUTPUT FROM COMPUTER PROGRAM

SQUARE ROOT OF M	PHI	I
4.41210	2.56308	11
11.39790	2.94017	5

Table A.E-1

$r = 1 \qquad q = 2.0$

$\sqrt{M}$	Φ^{*}	No. of Trials	Φ^{**}	No. of Trials	True Value
100.000	2.99972	5	2.99972	6	2.997
50.0000	2.99843	5	2.99843	6	2.9984
11.3979	2.94017	5	2.94017	5	2.9402
4.4121	2.56308	11	2.56334	14	2.5635

* Convergence test on $\sqrt{M}$ was $\pm$ 0.001

** Convergence test on $\sqrt{M}$ was $\pm$ 0.0001

APPENDIX F

DERIVATION OF INTEGRATED EQUATIONS FOR PACKED TOWER HEIGHT (INTEGRAL METHOD)

Derivations of the Hatta theory for absorption with an infinitely fast reaction in packed towers is given by Secor and Southworth[1] and Sherwood and Pigford[2] with the following results:

$$N_A = k_G P \qquad \text{for } q \geq q_c \qquad \text{(A.F-1)}$$

$$N_A = \frac{p/H + \frac{D_B}{D_A}\rho q}{\frac{1}{k_L^o} + \frac{1}{Hk_G}} \qquad \text{for } q \leq q_c \qquad \text{(A.F-2)}$$

where $$q_c = \frac{D_A k_G p}{D_A k_L^o \rho}$$

q_c has been termed the "critical concentration". If absorption takes place at constant temperature and constant total pressure into a solution in which the bulk concentration of B is above the critical

---

[1] R. M. Secor and R. W. Southworth, "Absorption With an Infinitely Rapid Chemical Reaction in Packed Towers," A.I.Ch.E. Journal, VII (1961), p. 705.

[2] T. K. Sherwood and R. L. Pigford, Absorption and Extraction, (2nd Edition; New York: McGraw-Hill, Inc., 1952), pp. 317-339.

value, the theory predicts the rate of absorption remains constant as q decreases to the critical value. The rate then falls off linearly with q as indicated by Equation (A.F-2), on the assumption other quantities in the equation remain constant. When component B is completely reacted, absorption occurs by physical solution of A.

In the top zone shown in Figure 17, the absorption is completely determined by gas phase resistance and the rate equation is

$$N_A a = k_G a P \ (y - 0) \qquad \text{(A.F-3)}$$

A material balance over a differential length of the tower is given by

$$N_A a = G_M \frac{dy}{dh} \qquad \text{(A.F-4)}$$

Assuming $(G_M/k_G aP)$ to be constant the integrated equation gives

$$h_s = \frac{G_M}{k_G a P} \ \ln \ y_3/y_4 \qquad \text{(A.F-5)}$$

For the interior-reaction zone the differential material balance, Equation (A.F-4) and the rate equation, Equation (A.F-2) are combined to give,

$$G_M \frac{dy}{dh} = \frac{p + \frac{D_B H \rho q}{D_A}}{\frac{1}{k_G a} + \frac{H}{k_L^o a}} \qquad \text{(A.F-6)}$$

$$= K_G a P \left[y + \frac{D_B H \rho q}{D_A P} \right]$$

It is convenient to define the Henry's law constant in terms of mole fractions as $m = \rho H/P$, which gives

$$G_M \frac{dy}{dh} = K_G aP \left[y + \frac{D_B mq}{D_A} \right] \qquad \text{(A.F-7)}$$

A material balance over a portion of the tower gives

$$q = q_c - \frac{G_M}{L_M} (y - y_3) \qquad \text{(A.F-8)}$$

Substituting Equation (A.F-8) into (A.F-7) yields

$$\frac{dy}{dh} = \frac{K_G aP}{G_M} \left[\left(1 - \frac{mG_M}{L_M} \frac{D_B}{D_A} \right) y + \frac{mq_c}{D_A} \frac{D_B}{D_A} \right.$$

$$\left. + \frac{mG_M}{L_M} \frac{D_B}{D_A} y_3 \right] \qquad \text{(A.F-9)}$$

Equation (A.F-9) is of the form

$$\frac{dy}{dh} = \frac{K_G aP}{G_M} (\alpha y + \beta) \qquad \text{(A.F-10)}$$

where α and β are constants. Separating the variables and integrating,

assuming $(G_M/k_G aP$ constant, one obtains

$$h_l = \frac{\frac{G_M}{K_G aP} \ln \left[\left(1 - \frac{mG_M}{L_M} \frac{D_B}{D_A}\right) \left[\frac{y_2 + \frac{mq_c}{D_A}\frac{D_B}{}}{y_3 + \frac{mq_c}{D_A}\frac{D_B}{}}\right] + \frac{mG_M}{L_M}\frac{D_B}{D_A}\right]}{\left(1 - \frac{mG_M}{L_M}\frac{D_B}{D_A}\right)} \qquad \text{(A.F-11)}$$

For physical absorption one uses Colburn's equation, namely

$$h_p = \frac{\frac{G_M}{K_G aP} \ln \left[\left(1 - \frac{mG_M}{L_M}\right) \left(\frac{y_1}{y_2}\right) + \frac{mG_M}{L_M}\right]}{\left(1 - \frac{mG_M}{L_M}\right)} \qquad \text{(A.F-12)}$$

The total tower height is

$$h = h_s + h_l + h_p$$

In order to use Equation (A.F-11) the value of q_c must be found in terms of material balances with the terminal concentration, y_1, y_4, and q_4. Using the definition of q_c with material balances, one gets,

$$q_c = \frac{\frac{D_A}{D_B}\frac{k_G}{k_L^o}\frac{PL_M}{\rho G_M} q_4 + \frac{D_A}{D_B}\frac{k_G}{k_L^o}\frac{P}{\rho} y_4}{1 + \frac{D_A}{D_B}\frac{k_G}{k_L^o}\frac{PL_M}{\rho G_M}} \qquad \text{(A.F-14)}$$

The application of these also require that y_2 be known; it is calculated by means of another material balance

$$y_2 = y_4 + \frac{L_M}{G_M} (q_4 - 0) \qquad \text{(A.F-15)}$$

The entire problem can be solved if y_1, y_4, and q_4 along with the other physical constants, mass transfer coefficients, and flow rates are known.

APPENDIX G

STATEMENT LIST OF COMPUTER PROGRAM FOR PACKED ABSORBER CALCULATIONS BY DIFFERENTIAL METHOD

```
$JCB            J.E.L.  REACTOR MODEL
      DIMENSION Y(500),CKG(500),Q(500),C(500),SMS(500),
     1EKG(500)
                CALL FPTRAP(-3)
1000  READ 13,XKG,XKL,DA,DB,XKF,XM
      READ 14,G,XL,AE,A,BB,P,N,T
1     READ 18,QP,SMT
      B=BB
      XKLO=XKL/AE*(30.5/3600.)
      R=SQRT(DB/DA)
      XN=N
      PUNCH 501
501   FORMAT(6X,11HGAS PHASE K,3X,12HLIQ. PHASE K,4X,
     110HSOLUBILITY)
      PUNCH 19,XKG,XKL,XM
19    FORMAT(3F15.2)
55    PUNCH 500
500   FORMAT(4X,6HHEIGHT,2X,8HLIQ CONC,2X,16HOUTLET GAS CONC.,
     12X,17HFRACTION ABSORBED)
     117HFRACTION ABSORBED)
5     H=(A-B)/XN
      KC=0
      DO 88 J=1,N
      XJ=J
      Y(J)=B+XJ*H
      Q(J)=QP-G/XL*(Y(J)-B)
C TEST FOR ZERO REACTANT CONCENTRATION
      IF(Q(J)) 71,4,4
71      KO=KO+1
      IF(KO-1) 72,72,73
72    XO=G/XL*(A-Y(J))
73    YS=(XO-G/XL*(A-Y(J)))*XM*3.46
C CALCULATE COEFFICIENT FOR PHYSICAL ABSORPTION
      CKG(J)=1./(1./XKG+XM/XKL)
      CKG(J)=CKG(J)*(Y(J)-YS)/Y(J)
      GO TO 88
C CALCULATE FOR CHEMICAL ABSORPTION
 4    K=0
C START ITERATIVE PROCEDURE FOR INTERFACIAL CONC CALCULATION
      C(1)=Y(J)/(XM*3.46)
2     K=K+1
      PHIA=1.+Q(J)/C(K)*R
       SM=SQRT(XKF*Q(J)*DA/18.)/XKLO
      IF(SM-SMT ) 110,110,111
C FOR LONG CONTACT TIME ASYMPTOTE SOLUTION IS USED
111   PHI=PHIA
      GO TO 101
C ITERATIVE SOLUTION FOR PHI AT A VALUE OF M
110   SMS(1)=SM
      I=0
100   I=I+1
      E=(ABS(SM/SMS(I)))**2.5
      PHI=PHIA-(PHIA-1.)/E
      YEY=1.129*SMS(I)
```

```
C CONSTRAINT ON SIZE OF ARGUMENT TO PREVENT OVERFLOW
      IF(YEY- 4.) 60,70,70
70    BZ=1.0
      GO TO 9
60    BZ=ERF(YEY)
9     SAS=ABS(SMS(I))
C CONSTRAINT ON SIZE OF SM TO PREVENT OVERFLOW
      IF(SAS-7.) 6,6,7
7     AZ=.000001
       GO TO 8
6     AZ=EXP(-1.274*SMS(I)**2)
8     SMS(I+1)=(PHI-3.14/(8.*SMS(I))*BZ+.5*AZ)/BZ
      TA=ABS(1.-SMS(I)/SMS(I+1))
      IF(T-TA) 100,100,101
101   X1=1./XKG
      X2=XM/(XKL*PHI)
      Z1=X1+X2
      EKG(K+1)=1./Z1
      EKG(1)=XKG
      CI=(XKG*Y(J)/(XKL*PHI*3.46))/(1.+(XKG*XM)/(XKL*PHI))
      D1=ABS(EKG(K+1)-EKG(K))
      IF(D1-P) 10,10,11
C ITERATE FOR VALUE OF CONC. UNTIL VALUE OF OVERALL COEFF.
C CONVERGES
11    C(K+1)=CI
      GO TO 2
10    CKG(J)=EKG(K+1)
88    CONTINUE
C NUMERICAL INTEGRATION FOR HEIGHT OF TOWER
      SUM2=0.0
      SUM4=0.0
      A1=1./(CKG(N)*A)
      B1=1./(CKG(1)*B)
      L=N-1
      M=N-2
      DO 20  I=1,L,2
20    SUM4=SUM4+1./(CKG(I)*Y(I))
      DO 30  J=2,M,2
30    SUM2=SUM2+1./(CKG(J)*Y(J))
      RESULT=H/3.*(A1+B1+2.*SUM2+4.*SUM4)
      HEI=G*RESULT
      FRAC=(A-B)/A
      PUNCH 16,HEI,QP,B,FRAC
C TEST HEIGHT OF TOWER AND ITERATE OUTLET CONC. UNTIL IT
C CONVERGES
      IF(HEI-1.7) 41,42,42
42    B=B+.00001
      GO TO 5
C LOWER LIQUID PHASE CONCENTRATION
41    QP=QP-.00002
90    B=B
      IF(QP-.00003) 1000,55,55
13    FORMAT(2F10.5,3E12.0,F10.5)
14    FORMAT(3F6.0,2F12.0,F10.5,I4,F10.5)
```

```
15      FORMAT(I4,4E10.5,I3,2F10.2,I3)
16      FORMAT(2F10.5,7X,F7.5,11X,F6.3)
18      FORMAT(E10.5,F10.5)
        END
$ENTRY
```

APPENDIX H

NUMERICAL ANSWERS FROM COMPUTER PROGRAM

GAS PHASE K	LIQ. PHASE K	SOLUBILITY
8.80	35.45	67.00
HEIGHT LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75149 0.CC030	0.C0020	0.957
1.72421 0.CC030	0.CC021	0.954
1.69820 0.C0030	C.00022	0.952
HEIGHT LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.70440 0.CC028	0.C0022	0.952
1.67947 0.CC028	0.CC023	0.950
HEIGHT LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.69202 0.C0026	0.C0023	0.950
HEIGHT LIQ CCNC	OUTLET GAS CONC.	FRACTION ABSORBED
1.71393 0.CC024	0.CC023	0.950
1.68978 0.C0024	0.00024	0.948
HEIGHT LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.72551 0.C0022	0.C0024	0.948
1.70209 0.CC022	C.C0025	0.946
1.67557 0.C0022	0.00026	0.943
HEIGHT LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.73658 0.CC020	0.00026	0.943
1.71450 0.CC020	C.C0027	0.941
1.69319 0.CC020	0.00028	0.939
HEIGHT LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.80051 0.CC018	0.00028	0.939
1.77924 0.CC018	C.C0029	0.937
1.75865 0.CC018	0.00030	0.935
1.73663 0.CC018	0.00031	0.933
1.71726 0.CC018	0.00032	0.930
1.69599 0.CC018	C.C0033	0.928
HEIGHT LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.87598 0.00016	0.00033	0.928
1.85640 0.CC016	C.C0034	0.926
1.83733 0.CC016	C.CC035	0.924
1.81874 0.CC016	0.00036	0.922
1.80C61 0.C0016	0.00037	0.920
1.78290 0.C0016	0.00038	0.917
1.76404 0.CC016	0.00039	0.915
1.74714 0.C0016	0.00040	0.913
1.73C62 0.C0016	0.00041	0.911
1.71446 0.CC016	C.00042	0.909
1.69864 0.CC016	C.CC043	0.907
HEIGHT LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.79682 0.00014	0.00055	0.880
1.78189 0.C0014	0.00056	0.878
1.76718 0.CC014	C.00057	0.876
1.75270 0.C0014	0.00058	0.874
1.73610 0.C0014	0.00059	0.872
1.72206 0.C0014	0.00060	0.870

1.70822	0.00014	0.00061	0.867
1.69459	0.00014	0.00062	0.865
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.74267	0.00012	0.00168	0.635
1.73229	0.00012	0.00169	0.633
1.72197	0.00012	0.00170	0.630
1.71171	0.00012	0.00171	0.628
1.70151	0.00012	0.00172	0.626
1.69137	0.00012	0.00173	0.624
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.74941	0.00010	0.00213	0.537
1.73709	0.00010	0.00214	0.535
1.72485	0.00010	0.00215	0.533
1.71269	0.00010	0.00216	0.530
1.70062	0.00010	0.00217	0.528
1.68827	0.00010	0.00218	0.526
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.76943	0.00008	0.00257	0.441
1.75414	0.00008	0.00258	0.439
1.73897	0.00008	0.00259	0.437
1.72394	0.00008	0.00260	0.435
1.70904	0.00008	0.00261	0.433
1.69426	0.00008	0.00262	0.430
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.78661	0.00006	0.00299	0.350
1.76695	0.00006	0.00300	0.348
1.74750	0.00006	0.00301	0.346
1.72827	0.00006	0.00302	0.343
1.70925	0.00006	0.00303	0.341
1.69044	0.00006	0.00304	0.339
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.84291	0.00004	0.00341	0.259
1.81479	0.00004	0.00342	0.257
1.78712	0.00004	0.00343	0.254
1.75990	0.00004	0.00344	0.252
1.73310	0.00004	0.00345	0.250
1.70672	0.00004	0.00346	0.248

GAS PHASE K	LIQ. PHASE K	SOLUBILITY
8.80	25.45	100.00

HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.78567	0.CC030	0.00020	0.957
1.75817	0.CC030	C.C0021	0.954
1.73194	C.C0030	C.00022	0.952
1.70686	0.C0030	0.00023	0.950
1.68285	0.CC030	0.00024	0.948
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.70554	0.C0028	C.00024	0.948
1.68238	0.00028	0.00025	0.946
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.71501	0.CC026	0.00025	0.946
1.69256	0.C0026	C.00026	0.943
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.73931	0.CC024	0.00026	0.943
1.71745	0.CC024	C.C0027	0.941
1.69637	0.C0024	C.00028	0.939
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.76358	0.CC022	0.C0028	0.939
1.74284	0.CC022	C.C0029	0.937
1.72278	0.C0022	C.00030	0.935
1.70334	0.00022	0.00031	0.933
1.68450	0.CC022	0.00032	0.930
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.78216	0.C0020	C.00032	0.930
1.76329	0.C0020	0.00033	0.928
1.74495	0.CC020	0.00034	0.926
1.72710	C.C0020	C.00035	0.924
1.70971	0.C0020	C.00036	0.922
1.69276	0.C0020	0.00037	0.920
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.83515	0.CC018	0.00037	0.920
1.82165	0.CC018	0.00038	0.917
1.80457	0.00018	0.00039	0.915
1.78787	0.00018	C.00040	0.913
1.77153	0.CC018	C.00041	0.911
1.75555	0.C0018	C.00042	0.909
1.73989	0.C0018	0.00043	0.907
1.72457	0.C0018	0.C0044	0.904
1.70954	0.C0018	0.00045	0.902
1.69481	0.C0018	C.00046	0.900
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.92123	0.00016	0.00046	0.900
1.90503	0.CC016	C.CC047	0.898
1.88911	0.00016	C.00048	0.896
1.87347	0.00016	0.00049	0.893
1.85811	0.CC016	0.00050	0.891
1.84299	0.CC016	C.00051	0.889
1.82813	0.C0016	0.00052	0.887
1.81351	0.00016	0.00053	0.885
1.79912	0.CC016	0.00054	0.883
1.78495	0.C0016	C.00055	0.880
1.77100	0.C0016	C.00056	0.878

1.75726	0.00016	0.00057	0.876
1.74372	0.00016	0.00058	0.874
1.73038	0.00016	0.00059	0.872
1.71724	0.00016	0.00060	0.870
1.70427	0.00016	0.00061	0.867
1.69148	0.00016	0.00062	0.865
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75841	0.00014	0.00083	0.820
1.74559	0.00014	0.00084	0.817
1.73334	0.00014	0.00085	0.815
1.72121	0.00014	0.00086	0.813
1.70921	0.00014	0.00087	0.811
1.69653	0.00014	0.00088	0.809
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.76018	0.00012	0.00122	0.735
1.74713	0.00012	0.00123	0.733
1.73467	0.00012	0.00124	0.730
1.72235	0.00012	0.00125	0.728
1.71016	0.00012	0.00126	0.726
1.69719	0.00012	0.00127	0.724
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75647	0.00010	0.00172	0.626
1.74275	0.00010	0.00173	0.624
1.72919	0.00010	0.00174	0.622
1.71578	0.00010	0.00175	0.620
1.70164	0.00010	0.00176	0.617
1.68852	0.00010	0.00177	0.615
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.78458	0.00008	0.00224	0.513
1.76658	0.00008	0.00225	0.511
1.74965	0.00008	0.00226	0.509
1.73295	0.00008	0.00227	0.507
1.71648	0.00008	0.00228	0.504
1.69983	0.00008	0.00229	0.502
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.80463	0.00006	0.00277	0.398
1.78209	0.00006	0.00278	0.396
1.75995	0.00006	0.00279	0.393
1.73821	0.00006	0.00280	0.391
1.71685	0.00006	0.00281	0.389
1.69515	0.00006	0.00282	0.387
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.84051	0.00004	0.00330	0.283
1.80772	0.00004	0.00331	0.280
1.77579	0.00004	0.00332	0.278
1.74467	0.00004	0.00333	0.276
1.71431	0.00004	0.00334	0.274
1.68468	0.00004	0.00335	0.272

GAS PHASE K	LIQ. PHASE K	SOLUBILITY
8.80	25.45	67.00
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.78502	0.00030	0.00020	0.957
1.75753	0.00030	0.00021	0.954
1.73130	0.00030	0.00022	0.952
1.70623	0.00030	0.00023	0.950
1.68222	0.00030	0.00024	0.948
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.70442	0.00028	0.00024	0.948
1.68126	0.00028	0.00025	0.946
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.71310	0.00026	0.00025	0.946
1.69067	0.00026	0.00026	0.943
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.73610	0.00024	0.00026	0.943
1.71427	0.00024	0.00027	0.941
1.69321	0.00024	0.00028	0.939
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75822	0.00022	0.00028	0.939
1.73753	0.00022	0.00029	0.937
1.71750	0.00022	0.00030	0.935
1.69811	0.00022	0.00031	0.933
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.79251	0.00020	0.00031	0.933
1.77316	0.00020	0.00032	0.930
1.75436	0.00020	0.00033	0.928
1.73608	0.00020	0.00034	0.926
1.71831	0.00020	0.00035	0.924
1.70099	0.00020	0.00036	0.922
1.68411	0.00020	0.00037	0.920
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.82344	0.00018	0.00037	0.920
1.80609	0.00018	0.00038	0.917
1.78915	0.00018	0.00039	0.915
1.77258	0.00018	0.00040	0.913
1.75638	0.00018	0.00041	0.911
1.74053	0.00018	0.00042	0.909
1.72502	0.00018	0.00043	0.907
1.70982	0.00018	0.00044	0.904
1.69492	0.00018	0.00045	0.902
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.90892	0.00016	0.00045	0.902
1.89273	0.00016	0.00046	0.900
1.87682	0.00016	0.00047	0.898
1.86120	0.00016	0.00048	0.896
1.84586	0.00016	0.00049	0.893
1.83078	0.00016	0.00050	0.891
1.81596	0.00016	0.00051	0.889
1.80137	0.00016	0.00052	0.887
1.78703	0.00016	0.00053	0.885
1.77291	0.00016	0.00054	0.883
1.75901	0.00016	0.00055	0.880
1.74532	0.00016	0.00056	0.878

1.73185	C.CC016	C.00057	0.876
1.71857	0.CC016	0.00058	0.874
1.70549	0.CC016	C.00059	0.872
1.69260	0.CC016	C.00060	0.870
HEIGHT	LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75128	0.00014	C.00080	0.826
1.73898	0.CC014	0.00081	0.824
1.72682	0.CC014	C.00082	0.822
1.71478	0.CC014	C.00083	0.820
1.70272	0.CC014	0.00084	0.817
1.69C94	0.CC014	C.00085	0.815
HEIGHT	LIC CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75348	0.CC012	C.00117	0.746
1.74115	0.CC012	0.00118	0.743
1.72856	0.CC012	0.00119	0.741
1.71650	0.CC012	C.00120	0.739
1.70455	0.CC012	C.00121	0.737
1.69272	0.00012	0.00122	0.735
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.75574	0.CC010	C.00165	0.641
1.74240	0.CC010	C.00166	0.639
1.72923	0.CC010	C.00167	0.637
1.71582	0.00010	0.00168	0.635
1.70294	0.CC010	C.00169	0.633
1.69C20	0.CC010	C.00170	0.630
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.79394	0.00006	0.00269	0.415
1.77271	0.CC006	C.00270	0.413
1.75183	0.CC006	C.00271	0.411
1.73C97	0.00006	C.00272	0.409
1.71C77	0.CC006	C.00273	0.407
1.69089	0.CC006	C.00274	0.404
HEIGHT	LIQ CONC	OUTLET GAS CONC.	FRACTION ABSORBED
1.83560	0.00004	0.00321	0.302
1.80523	0.CC004	0.00322	0.300
1.77557	0.CC004	C.00323	0.298
1.74662	0.00004	C.00324	0.296
1.71831	0.CC004	C.00325	0.293
1.69C61	0.CC004	0.00326	0.291

APPENDIX I

SAMPLE CALCULATIONS

A. Contact Time

System: CO_2 - H_2O

Run 1

Jet Length 3.441 cm.

Liquid Flow Rate 2.55 cc./sec.

Mean Diameter 1.14 mm. from Figure 10.

$$t' = \frac{\text{Volume of Jet Element}}{\text{Flow Rate}}$$

$$t' = \frac{(3.14)(.114 \text{ cm.})^2(3.441 \text{ cm.})}{(4)(2.55 \text{ cc./sec.})} = .0138 \text{ sec.}$$

$$1/\sqrt{t'} = 8.5 \text{ sec.}^{-1/2}$$

B. Mass Transfer Flux

System: CO_2 - H_2O

Run 1

Average Absorption Rate .0490 cc./sec.

Mean Diameter 1.14 mm. (see A above)

Jet Length 3.441 cm.

Transfer Area = (3.14)(.114 cm.)(3.441 cm.)

= 1.123 $cm.^2$

Average Flux = $\frac{\text{Absorption Rate}}{\text{Area}}$

$$N_{A,\ avg.} = \frac{.0490 \text{ cc./sec.}}{1.23 \text{ cm.}^2 \ (24{,}200 \text{ cc./gm. mole})}$$

$$= 1.63 \times 10^{-6} \text{ gm. mole/cm.}^2\text{-sec.}$$

C. Diffusion Coefficient from Single Point Calculation

System: CO_2 - H_2O

Run 1

Equation (3-20) shows the relationship between the average mass flux and the contact time.

$$N_A = 2\ (C_{A_i} - 0) \sqrt{\frac{D_A}{\pi t'}} \qquad (3\text{-}20)$$

The solubility of CO_2 in water is given in Chapter VI as,

$$C_{A_i} = 3.39 \times 10^{-5} \text{ gm. mole/cc.}$$

and in A and B above,

$$\bar{N}_A = 1.63 \times 10^{-6} \text{ gm. mole/cm.}^2\text{-sec.}$$

$$1/\sqrt{t'} = 8.5$$

Rearranging Equation (3-20) to solve for D_A;

$$D_A = \frac{\bar{N}_A^2 \pi t'}{4 (C_{A_i})^2} = \frac{(1.63 \times 10^{-6})^2 (3.14)(.0138)}{(4)(3.39 \times 10^{-5})^2}$$

$$D_A = 2.5 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$

D. Contact Time

System: Sodium Hydroxide - Methyl Mercaptan

Run 102

Liquid Flow Rate 2.55 cc./sec.

Jet Length 3.646 cm.

Mean Diameter 1.16 mm. from Figure 10

$$t' = \frac{\text{Volume of Jet Element}}{\text{Flow Rate}}$$

$$t' = \frac{.0386 \text{ cm.}^3}{2.55 \text{ cm.}^3/\text{sec.}} = .0151 \text{ sec.}$$

C. Mass Transfer Flux

System: Sodium Hydroxide - Methyl Mercaptan

Run 102

Average Absorption Rate .255 cc./sec.

Mean Diameter 1.16 mm.

(at liquid flow rate and jet length)

Jet Length 3.646 cm.

Transfer Area $\underline{1.33}$ $cm.^2$

$$\text{Average Flux} = \frac{\text{Absorption Rate}}{\text{Area}}$$

$$\bar{N}_A = \frac{.255 \text{ cc./sec.}}{1.33 \text{ cm.}^2} = \underline{0.192} \quad \frac{\text{cc.}}{\text{cm.}^2 \text{ sec.}}$$

F. Calculation of Liquid Phase Mass Transfer Coefficient

$\bar{N}_A = k_L (C_i - C)$, $C = 0$ from Equation (3-12)

$$k_L = \frac{\bar{N}_A}{C^*}$$

Run 102

$C_i = 2.45 \times 10^{-4}$ gm.mole/$cm.^3$ from Chapter VI, Section 1

$$k_L = \frac{.192 \text{ cm.}^3/\text{cm.}^2 - \text{sec.} \times 60 \text{ sec./min.}}{2.45 \times 10^{-4} \text{ gm.mole/cm.}^3 \times 24{,}200 \text{ cm.}^3/\text{gm.mole}}$$

$$k_L = 1.94 \text{ cm./min.}$$

G. Calculation of Height of Gas Phase Transfer Unit in Pilot Packed Tower: Basis Reference 51. (Jensen)

Gas Flow Rate $4.91 \frac{\text{lb. moles}}{\text{hr. ft.}^2}$

Pressure 1 atm.

Packed Height 1.7 feet

Fraction Absorbed .953

Rearranging Equation (5-48), $K_G a = \frac{G_M}{hP} \ln y_1/y_2$, for limiting case gas phase controlling

$$\frac{y_1 - y_2}{y_1} = 1 - y_2/y_1 = .953$$

$$y_1/y_2 = 21.1$$

$$K_G a = \frac{(4.91)}{(1.7)(1)} \quad \ln [21.1] = \frac{(4.91)(3.047)}{1.7}$$

$$K_G a = \underline{8.8} \ \frac{\text{lb. moles}}{\text{hr. ft.}^2 \text{ (atm.)}} \ \left(\frac{\text{ft.}^2}{\text{ft.}^3}\right)$$

$$[\text{Height of Transfer Unit}]_{\text{Gas}} \equiv H_G = \frac{G_M}{k_G a p}$$

For gas phase controlling

$$\frac{1}{K_G a} \cong \frac{1}{k_G a}$$

$$H_G = \frac{G_M}{K_G a P} = \frac{4.91}{(8.8)(1)} = .56 \text{ ft.}$$

H. Calculation of Height of Liquid Phase Transfer Unit in Pilot Packed Absorber

Gas Flow Rate 4.91 lb. moles/hr. - ft.^{2}

Liquid Flow Rate 3100 lb./hr. - ft.^{2}

Pressure 1 atm.

Packed Height 1.7 feet

Fraction Absorbed with Water .159

$$K_G a = \frac{GM}{hP} \ \ln y_1/y_2 = .501$$

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{M}{k_L^o a}$$

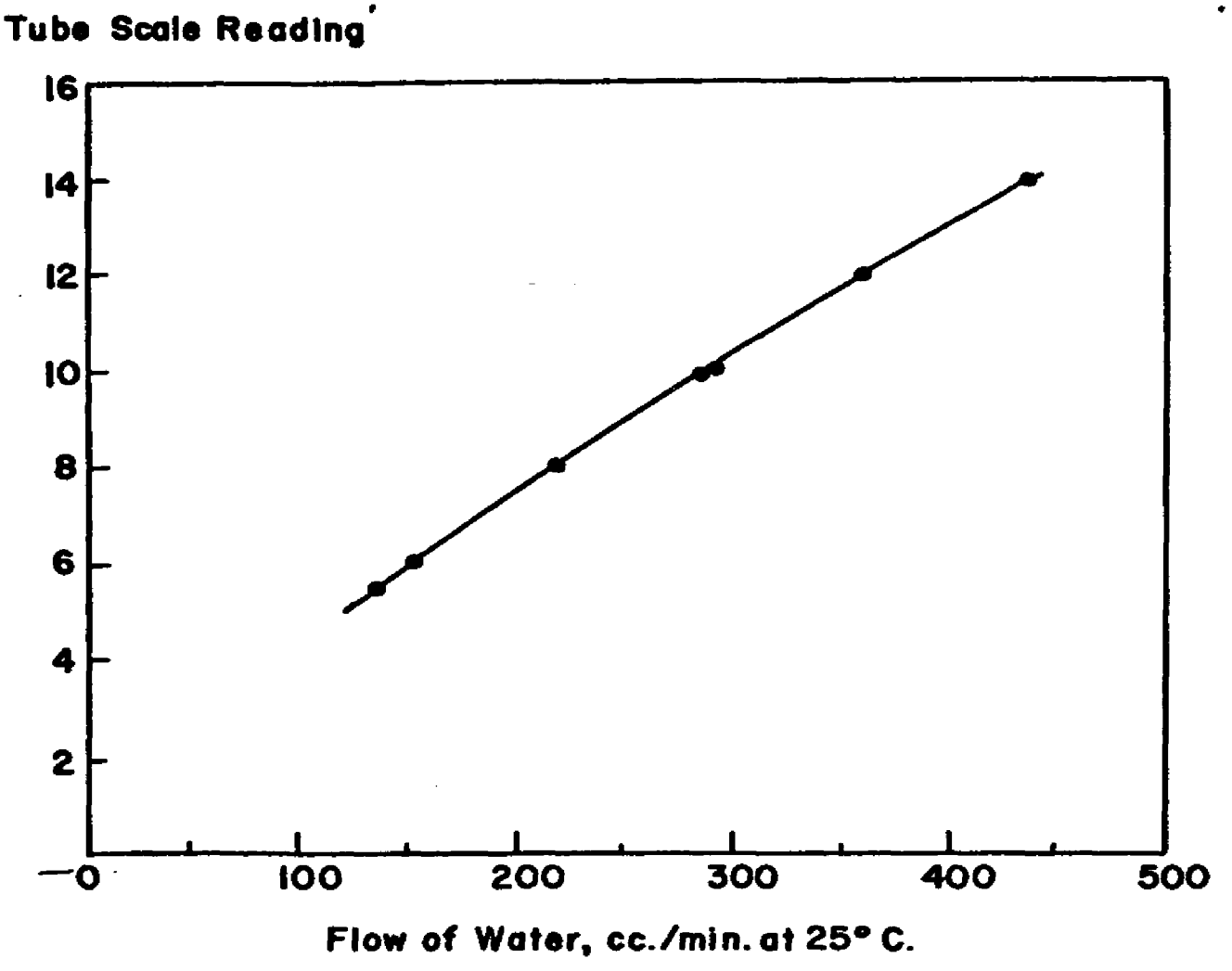
$$\frac{1}{.501} = \frac{1}{8.8} + \frac{67}{k_L^o a}$$

$$k_L^o a = 35.4 \ \frac{16 \text{ mole}}{\text{hr. ft.}^2 \ (16 \text{ mole/ft.}^3} \ \left(\frac{\text{ft.}^2}{\text{ft.}^3}\right)$$

Height of Liquid Transfer Unit $\equiv H_L$

$$H_L = \frac{1}{\rho k_L^o a} = \frac{3100}{(62.4)(35.4)} = \underline{1.4} \text{ ft.}$$

APPENDIX J, Rotameter Calibration of Fischer & Porter,
Tube FP-3/8-25-5
Float-3/8 CD



AUTOBIOGRAPHY

Josephy Earl Landry was born January 6, 1936 in St. Martinville, Louisiana. He attended St. Martin Parish schools and graduated from Breaux Bridge High School in 1954. He entered the University of Southwestern Louisiana in 1954 and graduated with a Bachelor of Science degree in Chemical Engineering.

After graduation he accepted a position as Research Chemical Engineer in Allied Chemical's Baton Rouge Development Laboratory and in January 1959 he began attending night graduate courses at Louisiana State University.

In June 1962, he accepted a position on the staff of the Louisiana State University Division of Engineering Research as a Research Associate in a project sponsored by the National Council for Stream Improvement (of the Pulp, Paper, and Paperboard Industries).

In August of 1963 he received the Master of Science degree in Chemical Engineering and is presently a candidate for the degree of Doctor of Philosophy in the Department of Chemical Engineering.

EXAMINATION AND THESIS REPORT

Candidate: Joseph Earl Landry

Major Field: Chemical Engineering

Title of Thesis: The Effect of A Second Order Chemical Reaction on the Absorption of Methyl Mercaptan in a Laminar Liquid Jet

Approved:

Jesse Coates
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Paul W. Merrill

Eugene W. Berg

Joe J. Berg

Arthur G. Keller

Date of Examination:

July 15, 1966